mg. of rose bengal in sufficient 95% ethanol to give a total volume of 280 ml. (0.02 *M* in palustric acid and 50 mg./l. in dye) was aerated and irradiated simultaneously in the 15-watt apparatus for 83 minutes (temp. 27–45°). At this point the photosensitized oxidation was essentially complete as indicated by a very small value of α at 266 mμ and $[\alpha]^{27}\mathrm{D}$ $-41.4°$. Aeration and irradiation were continued for an additional 20 minutes to ensure completeness of reaction. Essentially no change in α nor $[\alpha]\mathrm{D}$ was observed. No characteristic absorption was exhibited in the ultraviolet region of 220–320 mμ. To exactly one-half of the solution was added 1.12 g. of sodium hydroxide, dissolved by shaking (0.2 *M* in sodium hydroxide; 10:1 ratio of palustric acid sodium hydroxide); the alkaline solution was then refluxed for 10 minutes. Essentially no change was found in the ultraviolet absorption spectrum of the solution between 220–320 mμ and the optical rotation remained essentially unchanged at $[\alpha]^{27}\mathrm{D}$ -41.9. The solution was evaporated under reduced pressure to 40 ml., water (50 ml.) added, drying continued to a volume of 40 ml., water (20 ml.) added, and the solution reduced to a final volume of 50 ml. Glacial acetic acid (2.4 ml.) was added and the acidic solution extracted with ether. The ethereal extracts were combined, taken to dryness under reduced pressure, and dried over potassium hydroxide and Drierite *in vacuo;* yield 0.79 g. (84%). This was dissolved in acetone, 0.40 ml. of freshly distilled cyclohexylamine added, and the precipitate which formed collected by filtration, washed with pentane and dried; yield 1.01 g. (99% from acid), $[\alpha]^{27}\mathrm{D}$ $-24.5°$ (*c* 1.0% in 95% ethanol).

The other half of the original solution of palustric acid photoperoxide was concentrated under reduced pressure and water added. The oil which formed solidified and was collected by filtration and dried; yield 0.79 g. (84%). This was dissolved in acetone, 0.40 ml. freshly distilled cyclohexylamine added, the precipitate collected by filtration, and dried; yield 0.96 g. (94% from acid), $[\alpha]^{27}\mathrm{D}$ $-25.0°$ (*c* 1.0% in 95% ethanol).

The infrared absorption spectra of both salts and the ultraviolet absorption spectra between 220–320 mμ of both salts were found to be essentially identical. The infrared spectra exhibited no O–H stretching band in the 3 μ region and no C=O stretching bands in the 5.8 and 8.8 μ regions. The carboxylate ion stretching band was observed at 6.5 μ.

Nuclear Magnetic Resonance Absorption Spectra.—The nuclear magnetic resonance absorption spectra were run in a Varian high-resolution spectrometer, operating at 56.4 m.c. Both compounds were run as saturated solutions in carbon tetrachloride. The chemical shifts obtained, expressed as frequency shifts from benzene as an internal standard in parts per million of the operating frequency, are: palustric acid: olefinic hydrogen, +2.0; carboxylic hydrogen, −4.8; hydrogen on saturated carbons, +4.8 to +6.4 with strongest peaks at +5.2 and +6.1. 7,13-Peroxido-$\Delta^{8(14)}$-dihydroabietic acid: olefinic hydrogen, +1.86; carboxylic hydrogen, −1.82; hydrogens on saturated carbons, +4.2 to +6.4, with strongest peak at 6.21.

Acknowledgment.—The authors wish to express their appreciation to L. E. Brown, Instrumentation and Analysis Group, Southern Utilization Research and Development Division, for the elemental analyses; to Dr. Wallace S. Brey of the University of Florida (Gainesville) for the determination and interpretation of the nuclear magnetic resonance absorption spectra; and to G. S. Fisher of the Naval Stores Research Station for helpful discussions during the course of the work. References to specific products of commercial manufacture are for illustration only and do not constitute endorsement by the U. S. Department of Agriculture.

OLUSTEE, FLA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Reaction of Phenyl Radicals with Carbon Monoxide; Some Observations on the Induced Decomposition of Benzoyl Peroxide[1]

BY CHEVES WALLING AND EMANUEL S. SAVAS[2]

RECEIVED AUGUST 26, 1959

The reaction of phenyl radicals with carbon monoxide has been demonstrated by decomposing benzoyl peroxide under CO pressure in benzene, cyclohexane and carbon tetrachloride solution. In every case, yields of products arising from phenyl radical attack on solvent are reduced and benzoic anhydride is produced by what is believed to be an induced decomposition of peroxide by benzoyl radicals. Benzoic anhydride is similarly formed when benzoyl peroxide is decomposed in benzaldehyde under N_2. In the CO reaction in CCl_4, benzoyl chloride is also an important product. As a result of this and previous work, it is concluded that in decompositions of benzoyl peroxide giving rise to substituted benzoic acids these products are the result of induced decomposition involving *simultaneous* radical attack on the aromatic ring and scission of the O–O bond, giving a benzoyloxy radical and a metastable intermediate which rearranges to the acid. This intermediate is suggested as an α-lactone of 1-hydroxycyclohexadienecarboxylic acid. Experiments with ring-deuterated benzoyl peroxide indicate that radical attack and migration of a ring hydrogen are not concerted processes.

The loss of carbon monoxide from acyl free radicals is a well established process in the gas phase

$$\mathrm{R{-}\dot{C}O} \rightleftarrows \mathrm{R\cdot + CO} \qquad (1)$$

thermal and photochemical decomposition of aldehydes and ketones,[3] and also occurs in the liquid phase, notably in the radical chain decarbonylation of aldehydes.[4] In the case of the acetyl radical, Cramer[5] has reviewed thermochemical data and concluded that $\Delta H = 15 \pm 3$ kcal., $E_a = 16 \pm 3$ kcal. for reaction 1 proceeding to the right in the gas phase. Although (1) becomes less endothermic when R · is a highly resonance-stabilized radical,[6] it is evident that the reverse reaction, addition of CO to a hydrocarbon radical, should be a relatively exothermic, low activation energy process. A clear-cut case of such addition is provided by the copolymerization of carbon monoxide and ethylene,[7] and additional examples involving more complex

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[1] Taken from the Ph.D. Dissertation of Emanuel S. Savas, Columbia University, 1960. Support of this work by the Office of Ordnance Research, U. S. Army is gratefully acknowledged.

[2] Eugene Higgins Fellow, 1955–1956; Quincy Ward Boese Fellow 1957–1958.

[3] E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954.

[4] Work through 1956 on this and related reactions discussed here is reviewed by: C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 273–285.

[5] R. Cramer, THIS JOURNAL, **79**, 6215 (1957).

[6] Thus, the decarbonylation of trimethylacetaldehyde occurs readily at room temperature; *cf.* J. B. Conant, C. N. Webb and W. C. Mendum, *ibid.*, **51**, 1246 (1929).

[7] M. M. Brubaker, D. D. Coffman and H. H. Hoehn, *ibid.*, **74**, 1509 (1952).

chains have also been described.[8] The back reaction of (1) is favored by low temperatures, and it has recently been found that significant reaction of alkyl radicals with CO may occur near room temperature at CO pressures as low as one atmosphere.[9,10]

The reaction of phenyl radicals with CO appeared to us as a particularly favorable case for observing such addition, since the phenyl radical is highly reactive, and reaction should derive further driving force by resonance stabilization of the resulting benzoyl radical. Accordingly we have investigated the effect of CO on the products obtained from the decomposition of benzoyl peroxide in three solvents, with results clearly indicating the anticipated reaction. In the course of this work, we have also reached significant conclusions concerning the nature of the induced decomposition of benzoyl peroxide.

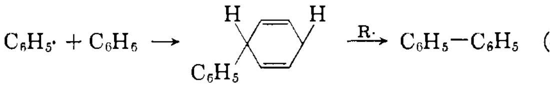
Results and Discussion

A. Reactions in Benzene.—Results of our study of the decomposition of 0.10 *M* solutions of benzoyl peroxide in benzene in the presence and absence of CO at 70 and 100° are listed in Table I. Products obtained in the absence of CO are essentially those described in the literature and are believed[11] to arise *via* the sequence

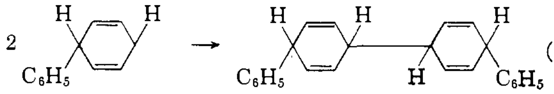
$$C_6H_5CO{-}O{-}O{-}COC_6H_5 \longrightarrow 2C_6H_5COO\cdot \quad (2)$$

$$C_6H_5COO\cdot + RH \longrightarrow C_6H_5COOH \quad (3)$$

$$C_6H_5COO\cdot \longrightarrow C_6H_5\cdot + CO_2 \quad (4)$$


(5)

Lynch and Pausacker[12] have suggested that the quaterphenyl is produced by the sequence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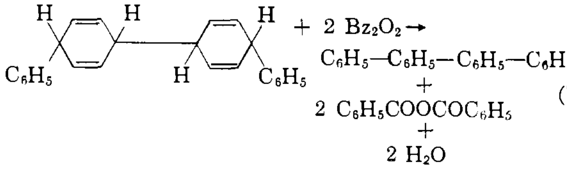
(7)

While reaction 6 appears very plausible and such products have been recently isolated,[13] our failure to detect benzoic anhydride in our CO-free experiments confirms previous results[11,14] and makes it likely that (7) should be replaced by some other dehydrogenation process.

TABLE I

EFFECT OF CO ON THE DECOMPOSITION OF 0.1 *M* BENZOYL PEROXIDE IN BENZENE

		Products, moles/mole peroxide				
CO[a]	*T*, °C.	Quaterphenyl[b]	Diphenyl	Acid	Anhydride	Ester
0	70	0.017	0.43	0.38	<0.01	0.12
0	70	.008		.34		.12
0	100	.010	.37	.43	<.01	.03
0	100	+	.46	.37		.11
2500	70	−	.09	.51	.33	.21
1900	70	−		.47	.28	
1900	70	+	.09	.64		.22
2610	100	−	.08	.66	.30	
1900	100	−	.08	.40		.31

[a] Initial pressure of CO in lb./sq. in. [b] + indicates qualitative presence, − absence.

In the presence of CO_2 yields of biphenyl are sharply reduced, and those of quaterphenyl eliminated, while benzoic anhydride becomes a prominent product. The elimination of polyphenyls certainly indicates the effective scavenging of phenyl radicals by the expected carbonylation reaction

$$C_6H_5\cdot + CO \longrightarrow C_6H_5\dot{C}O \quad (8)$$

and the benzoic anhydride, in turn, might arise by either a coupling reaction, *e.g.*

$$C_6H_5CO_2\cdot + C_6H_5\dot{C}O \longrightarrow C_6H_5CO{-}O{-}COC_6H_5 \quad (9)$$

or an induced decomposition of further peroxide[15]

$$C_6H_5\dot{C}O + C_6H_5CO{-}O{-}O{-}COC_6H_5 \longrightarrow C_6H_5CO{-}O{-}COC_6H_5 + C_6H_5CO_2\cdot \quad (10)$$

We believe that (10) is the major path of anhydride formation, both because yields of acid are not decreased in the presence of CO as required by (9), and because of the experiments discussed below and in sections B and C.

Benzoyl radicals can also be produced by decomposing benzoyl peroxide in the presence of benzaldehyde *via* the step

$$C_6H_5COO\cdot + C_6H_5CHO \longrightarrow C_6H_5COOH + C_6H_5\dot{C}O \quad (11)$$

as shown by Rust, Seubold and Vaughan.[16] We have compared the kinetics of the decomposition in benzene, benzene containing 0.1 *M* benzaldehyde, and in pure benzaldehyde with results shown in Fig. 1.[17] The data indicate a moderate acceleration in the presence of the aldehyde, which appears statistically significant even in the 0.1 *M* solution. Titration of a reaction mixture in pure benzaldehyde by the method used in Table I also indicated the presence of at least 10% benzoic anhydride, so we believe that there is good evidence for the sequence (10)–(11) even though chains are rather short.[18]

Table I also indicates a significant increase in the yields of ester obtained in the presence of CO.

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[8] T. L. Cairns, D. D. Coffman, R. Cramer, A. W. Larchar and B. C. McKusick, THIS JOURNAL, **76**, 3024 (1954); R. E. Foster, A. W. Larchar, R. D. Lipscomb and B. C. McKusick, *ibid.*, **78**, 5606 (1956); J. C. Sauer, *ibid.*, **79**, 5314 (1957).

[9] D. D. Coffman, R. Cramer and W. E. Mochel, *ibid.*, **80**, 2882 (1958).

[10] C. Walling, O. Basedow and E. S. Savas, unpublished work.

[11] *Cf.* reference 4, pp. 474–491.

[12] B. M. Lynch and K. H. Pausacker, *Australian J. Chem.*, **10**, 40 (1957).

[13] D. F. DeTar and R. A. J. Long, THIS JOURNAL, **80**, 4742 (1958).

[14] S. R. Rafikov and V. S. Kudinova, *Doklady Akad. Nauk S.S.S.R.*, **87**, 987 (1952).

[15] The question whether displacement in (10) occurs on carbonyl or peroxide oxygen is discussed further in section D below.

[16] F. F. Rust, F. H. Seubold and W. E. Vaughan, THIS JOURNAL, **70**, 3256 (1948).

[17] Several attempts were also made to study directly the kinetics of peroxide decomposition under CO. At one atmosphere, no significant effect was found. At higher pressures, difficulties in temperature control and the presence of traces of O_2 led to inconclusive and irreproducible results.

[18] The induced reaction in aliphatic aldehydes might be expected to be faster because of the greater rate of the step analogous to (11).[4]

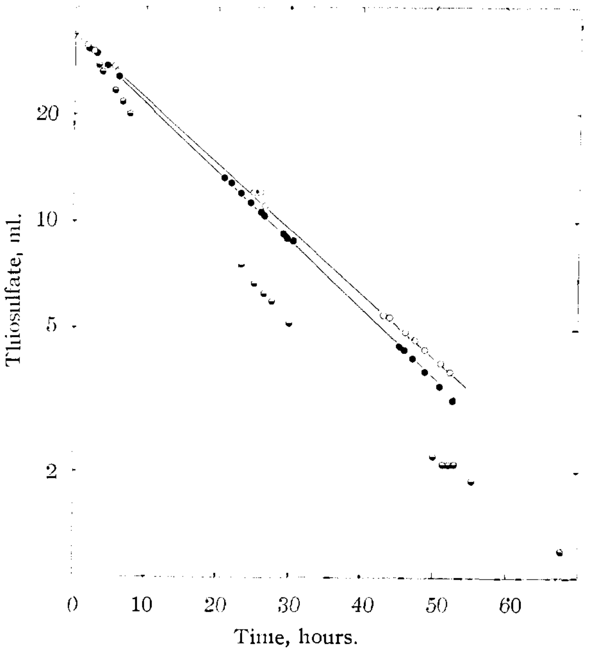

Fig. 1.—Effect of benzaldehyde on the decomposition of 0.1 *M* benzoyl peroxide in benzene at 70°: open circles, benzene alone; solid circles, 0.1 *M* benzaldehyde; semi-solid circles, benzaldehyde alone.

The structure of these esters were not determined in detail, but the increase is believed due to the presence of traces of oxygen in the CO employed, and is considered further in section B below.

Finally, aldehydes or ketones might be expected products from carbonyl radical reactions. Examination of the residues from a CO experiment showed an infrared peak at 6.03 μ characteristic of an aromatic ketone, and chromatography yielded approximately 1% of *p*-phenylbenzophenone, but no benzophenone.

B. **Reactions in Cyclohexane.**—Results obtained by decomposing 0.1 *M* solutions of benzoyl peroxide in cyclohexane at 70° are listed in Table II.

TABLE II

EFFECT OF CO ON THE DECOMPOSITION OF 0.1 *M* BENZOYL PEROXIDE IN CYCLOHEXANE AT 70°

		—Products, moles/mole peroxide—		
CO[a]	Benzene	Anhydride	Acid	Ester
0	0.71	0	1.07	0.03
0	.66	0	1.07	.04
15		0	1.08	
465	.52	0.27	0.79	.15
725[b]	.46	.61	.41	.02
1000	.36	.31	.73	.26
1500	.31	.54	.47	.10
2375	.16	.17	1.04	.45
2425	.18	.47	0.72	.45
2835	.17	.38	.64	.43
3215	.15	.39	.60	.40
3275	.18	.25	.92	
3325	.15	.46	.56	.41
4035	.15	.43	.68	.34

[a] Initial pressure, lb./sq. in. [b] Oxygen-free CO.

Again, acid anhydrides are a significant product of the reaction in the presence of CO at pressures as low as 465 lb./sq.in., although not at atmospheric pressure, and yields of benzene are reduced.

In our analytical scheme, free acids are first extracted with bicarbonate and the anhydrides then converted to acids by mild hydrolysis. In the absence of CO, the original free acids are largely (72% in a typical experiment) substituted benzoic acids together with benzoic acid. These substituted acids have been shown by Hermans and Van Eyk[19] to consist principally of cyclohexylbenzoic acids, and, as discussed in section D, are the products of induced decomposition. From reactions run in the presence of CO only negligible amounts of these substituted acids are isolated, the free acids being primarily benzoic acid together with some cyclohexanecarboxylic acid. The anhydride fraction also yields benzoic and considerable cyclohexanecarboxylic acids, indicating that it contains approximately 20% of mixed benzoic cyclohexanecarboxylic anhydride. We believe that the cyclohexanecarboxylic acid in the free acids also comes from slight hydrolysis of this anhydride, and have observed that, in reaction mixtures which are allowed to stand in stoppered flasks at room temperature, the anhydride content slowly drops while that of the free acid rises. Such partial hydrolysis would also account for the fact (Table II) that in presumably identical runs the sum of acid plus anhydride remains relatively constant although their ratio varies.

All of the products described above are consistent with a scheme in which (a) cyclohexane and CO compete for phenyl radicals, but the rate of phenyl radical attack on cyclohexane is high enough so that some benzene is produced even at the highest CO pressure; (b) cyclohexyl radicals are produced by attack of both $C_6H_5CO_2\cdot$ and C_6H_5 radicals on cyclohexane; (c) cyclohexyl radicals are essentially quantitatively carbonylated

$$C_6H_{11}\cdot + CO \longrightarrow C_6H_{11}CO \qquad (12)$$

This eliminates induced decomposition of peroxide *via* attack of cyclohexyl radicals (which would give rise to substituted benzoic acids). Instead, the radical produced in (12) attacks peroxide to give mixed anhydride

$$C_6H_{11}\dot{C}O + C_6H_5CO{-}O{-}O{-}COC_6H_5 \longrightarrow C_6H_{11}CO{-}O{-}COC_6H_5 + C_6H_5CO_2\cdot \qquad (13)$$

As in the case of reactions in benzene, experiments in the presence of CO showed significantly increased yields of ester. Although hydrolysis of the ester fraction gave solely benzoic and cyclohexanecarboxylic acids, the esters themselves were chiefly resinous materials of high molecular weight, from which a small amount of phenyl benzoate plus a crystalline material, m.p. 281–285°, with the approximate composition of tetrahydroxybenzene tetrabenzoate could be isolated. At this point in the work, it was realized that the esters might arise from oxidation reactions due to the traces of O_2 (approximately 0.2%) in the CO employed. Fortunately a supply of effectively O_2-free CO became available, and one experiment with this material gave essentially no ester, and it is worth noting that a plot of ester yield *vs.* oxygen concentration in our

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[19] P. H. Hermans and J. Van Eyk, *J. Polymer Sci.*, 1, 407 (1946).

systems (calculated from the CO pressure and its approximate oxygen concentration) is roughly linear, 1–2 millimoles of ester being produced per millimole O_2 present.

C. Reactions in Carbon Tetrachloride.—The results of our experiments on the decomposition of benzoyl peroxide in carbon tetrachloride solution appear in Table III. Oxygen-free CO was employed in all runs, and since only traces of esters could be detected in the products, ester yields are not included. The drop in yield of chlorobenzene in the presence of CO again points to the scavenging of phenyl radicals, but the resulting benzoyl radicals are now chiefly converted to benzoyl chloride by reaction with solvent.

TABLE III

EFFECT OF CO ON THE DECOMPOSITION OF 0.2 *M* BENZOYL PEROXIDE IN CCl_4 AT 70°

	Products, moles/mole peroxide					
CO[a]	C_6H_5Cl	C_6H_6	Acid[b]	Benzoyl chloride	Anhydride	C_2Cl_6
0	1.70	0.06	0.18	0	0	0.56
2200	0.44	.13	.06	0.85	0.23	.71
780	.73	.07	.17	.89	.02	.66

[a] Initial pressure (lb./sq. in.). [b] *p*-Trichloromethylbenzoic acid.

$$C_6H_5\dot{C}O + CCl_4 \longrightarrow C_6H_5COCl + \cdot CCl_3 \quad (14)$$

As in the absence of CO, the $\cdot CCl_3$ radicals produced undergo dimerization or, to a lesser extent, attack peroxide to give *p*-trichloromethylbenzoic acid. We were able to obtain no evidence for any reaction of $\cdot CCl_3$ radicals with CO, although our material balances in these experiments seem very good, accounting for at least 95% of the phenyl groups from the peroxide.[20]

D. Some Observations on the Induced Decomposition of Benzoyl Peroxide.—At the concentrations of peroxide at which the experiments described in previous sections were carried out, Nozaki and Bartlett's analysis[21] indicates that a considerable portion of the decomposition is by an induced reaction, and indeed we have used such an induced process to account for the formation of acid anhydrides in the presence of CO. We will now consider the induced decomposition in the absence of CO, drawing some conclusions as to its nature which we believe have not previously been recognized. In particular we will consider the reaction in cyclohexane, although our conclusions appear to apply to a number of other solvents as well.

The products obtained in cyclohexane have been studied by several workers, and product compositions reported by Hermans and Van Eck,[19] Swain, Schaad and Kresge[22] and in this paper are summarized in Table IV. The amount of induced reaction is estimated from Nozaki and Bartlett's rate constants, and since it accounts for most of the decomposition in approximately 0.1 *M* solution must also account for the major products, benzene and substituted benzoic acids. Swain's results have led him to the conclusion[22] that cyclohexyl radicals are chain carriers in the induced decomposition, so that the benzene is easily accounted for by the step

TABLE IV

PRODUCTS OF DECOMPOSITION OF BENZOYL PEROXIDE IN CYCLOHEXANE (IN MOLES/MOLE PEROXIDE)

	Hermans[19]	Swain[22]	This paper
$[Bz_2O_2]$, *M*	0.0825	0.003	0.100
T, °C.	79.8	91.1	70.0
Benzoic acid	0.35	0.52	0.3
Benzene	.52	1.11	.69
Esters	.03	0.014	.03
Subst. benzoic acids	.65	....	.75
% C_6H_5's accounted for	79	83	90
% induced decompn.	59	20	75

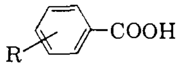
$$C_6H_5\cdot + C_6H_{12} \longrightarrow C_6H_5H + C_6H_{11}\cdot \quad (15)$$

The question of the reaction path by which the substituted benzoic acids are produced is more puzzling and has not heretofore been answered. In fact the only investigators who have clearly identified their formation with the *induced* decomposition have been DeTar and Weis,[23] and, as we shall see, their formulation appears inconsistent with experiment.

It is our proposal that *the substituted benzoic acids formed in the induced decomposition of benzoyl peroxide arise from a concerted process in which addition to the aromatic ring takes place concurrently with the scission of the O–O bond in the peroxide to give a metastable non-radical product and a benzoyloxy radical*

$$R\cdot + C_6H_5CO{-}O{-}O{-}COC_6H_5 \longrightarrow X + C_6H_5COO\cdot \quad (16)$$

This intermediate, for which we can only suggest a tentative structure, then rearranges to the substituted acid

X →

(17)

Two sorts of evidence support this interpretation. First, the mere existence of an induced reaction, in which relatively stable secondary alkyl radicals attack an aromatic system, implies some additional driving force which we believe to be the concurrent breaking of the O–O bond. Somewhat more quantitatively (although the structure of the product is merely assumed to be similar) the transfer constants of styrene with a whole variety of aromatic compounds is of the order of 10^{-5}, while that with benzoyl peroxide is 6×10^{-2},[24] so that clearly the reactions are of a different sort. Second, the formation of substituted benzoic acids, but no cyclohexylbenzene indicates that the reaction product of (16) cannot be a substituted benzoyloxy radical or similar species since this should undergo at least partial decarboxylation. Such an intermediate has been proposed by DeTar and Weis,[23] who have suggested the process illustrated in reaction (18) as the induced decomposition. We believe this interpretation is untenable for the reason just given.

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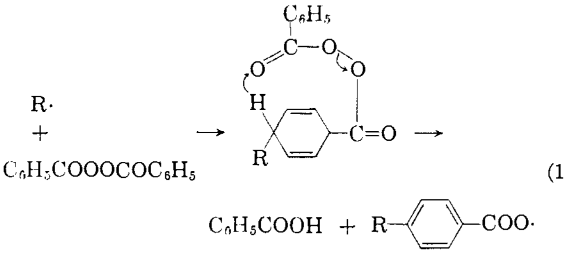
[20] The balance must represent some unidentified dehydrogenated product equivalent to the benzene formed.

[21] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

[22] C. G. Swain, L. J. Schaad and A. J. Kresge, *ibid.*, **80**, 5313 (1958).

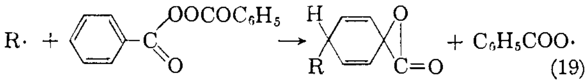
[23] D. F. DeTar and C. Weis, *ibid.*, **78**, 4296 (1956).

[24] F. R. Mayo, R. A. Gregg and M. S. Matheson, *ibid.*, **73**, 1691 (1951). The possibility that the transfer involves attack on oxygen cannot be excluded, and in fact most workers have probably considered this to be the case. This point is considered further below.



(18)

Turning now to the possible structure of the intermediate X, a possible formulation of (16) is



(19)

The facile rearrangement of the α-lactone product could well explain its non-isolation up to the present. A similar formulation could give rise to an *o*-substituted benzoic acid, but not a *m*-substituted one. In contrast, radical attack on aromatic systems by non-concerted processes give rather random mixtures, usually with considerable *m*-substitution.[11] As far as we know, only *o*- and *p*-substituted benzoic acids have been detected from the decomposition of benzoyl peroxide in cyclohexane[19] or other solvents.

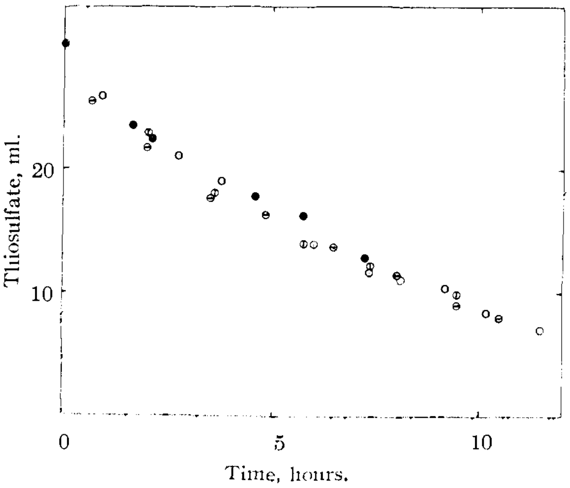
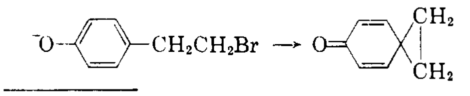


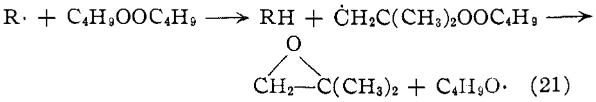
Fig. 2.—Effect of deuteration on decomposition of 0.1 *M* benzoyl peroxide in cyclohexane at 70°: open and closed circles, undeuterated peroxide (two runs); barred circles, deuterated peroxide (two runs).

Reaction 19 is offered without further direct proof and is only one of several possible alternatives. However, it has a number of analogies in the chemistry of both polar and free radical reactions. An α-lactone is considered to be a transient intermediate in the solvolysis of α-bromopropionate anion,[25] and a compound rather similar to the product of (19) has been isolated from the solvolysis of *p*-(β-bromoethyl) phenoxide ion[26]



(20)

Finally, the induced decomposition of undiluted *t*-butyl peroxide gives rise to isobutylene oxide[27]



$$R\cdot + C_4H_9OOC_4H_9 \longrightarrow RH + \dot{C}H_2C(CH_3)_2OOC_4H_9 \longrightarrow \overset{O}{CH_2 - C}(CH_3)_2 + C_4H_9O\cdot \quad (21)$$

Although there is no evidence that the two over-all steps are concerted, O–O bond breaking and ring formation must be concerted processes.

We have also considered the possibility that hydrogen migration is also concerted with radical attack on the aromatic ring and O–O bond scission to give substituted benzoic acids directly without an intermediate such as the α-lactone. Such a path requires a rather distorted transition-state for *p*-substitution, but could be detected by comparing the decomposition of benzoyl peroxide and ring deuterated peroxide under conditions where the decomposition is chiefly induced. We have carried out such an experiment with 0.1 *M* peroxide in cyclohexane, observing no isotope effect on the reaction rate, Fig. 2, or any increased concentration of deuterium in the remaining peroxide after partial reaction. However, the experiment was not entirely satisfactory since the peroxide proved to be incompletely deuterated, and a k_H/k_D ratio of under 1.5 would not have been detected. Nevertheless, the absence of any isotope effect of this magnitude would seem to rule out any concerted hydrogen transfer occurring in the transition state, and is thus further support for a metastable intermediate.

If our formulation is correct, it accounts for a major portion of the induced decomposition in a number of other solvents as well as cyclohexane. Thus *p*-trichloromethylbenzoic acid is an important product in carbon tetrachloride, both from our own and earlier work,[28] some phenylbenzoic acids are produced in benzene, and *o*- and *p*-carboxyphenylacetic acids in acetic acid. On the other hand, the elegant work of Cass[29] has shown that the very rapid induced decomposition in ethers involves attack on oxygen.[30] The similar fast reaction in alcohols appears to follow the same path,[31] as does the reaction with acyl radicals to give anhydrides described in this paper. This change in point of radical attack appears to be associated with radicals having particularly strong electron-donor properties, and as was pointed out some years ago,[32] their facile attack on an electronegative oxygen may be aided by charge transfer structures in the transition state. These structures would be less available if attack occurs on the aromatic ring.

Experimental

Materials.—Benzoyl peroxide was purified by dissolving Amend Drug and Chemical Co. C. P. grade material in chloroform and precipitating with two volumes of methanol.

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[25] S. Winstein, THIS JOURNAL, **61**, 1635 (1939).

[26] S. Winstein and R. Baird, *ibid.*, **79**, 756 (1957).

[27] E. R. Bell, F. F. Rust and W. E. Vaughan, *ibid.*, **72**, 337 (1950).

[28] For a summary with pertinent references to products in a variety of solvents, *cf.* A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 85.

[29] W. E. Cass, THIS JOURNAL, **69**, 500 (1947).

[30] Recent work using O^{18}-labeled peroxide shows that attack is on peroxide rather than carbonyl oxygen, R. B. Denney, private communication.

[31] P. D. Bartlett and K. Nozaki, THIS JOURNAL, **69**, 2299 (1947).

[32] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 269 (1950).

Purity by titration was over 99%. **Benzene**: analytical reagent grade material was dried and stored over sodium wire. **Cyclohexane**: Eastman Kodak Co. spectro grade and white label material dried over sodium wire gave identical results. Unlike the material described by Swain,[22] they did not decompose a significant amount of peroxide in 0.03 *M* solution at 25°. Carbon tetrachloride was distilled through an 18 in. column and the center fraction used.

Reactions under carbon monoxide were carried out in a steel hydrogenation bomb with glass liner mounted on a shaker assembly and containing either 200 or 400 ml. of solution. The system was flushed several times with CO and then charged to the desired pressure before heating and shaking were started. Reactions were run for 70–90 hours (adequate time for complete reaction) and temperature control was ±4°.

Control experiments were run on 200 ml. of solution in a glass flask under nitrogen, immersed in a 70° thermostat. Reaction time was again 70–90 hours. In kinetic runs samples were withdrawn periodically and titrated with thiosulfate after adding iodide and acetic acid in the usual manner.

Products from Benzene Experiments.—Reaction mixtures from CO reactions were dark reddish-brown (presumably due to oxidation by traces of O_2 in the CO), significantly darker than controls. In working up, most of the solvent was first removed by distillation through an 18-in. helix-packed column. Ether was added and the insoluble quaterphenyl removed by filtration; m.p. from nitrobenzene 316° (uncor.), reported 320°. Acids were next determined by extraction with several portions of bicarbonate, acidifying the extract, re-extracting into ether, evaporating and titrating with 0.05 *N* NaOH. Blank experiments with benzoic acid indicated an accuracy of ±2%.

Anhydride was next determined by evaporating the remaining original ether solution above and refluxing 3 hours with 0.109 *N* H_2SO_4. The acids produced were then extracted and determined as above. Blank experiments showed this technique to give 95–100% hydrolysis of benzoic anhydride, but only 2% of phenyl benzoate. Although the ether solution before hydrolysis showed infrared peaks at 5.58 and 5.80 μ characteristic of benzoic anhydride, and the hydrolysis product was identified as benzoic acid, it should be pointed out that benzoic anhydride was actually isolated and identified as such in subsequent experiments in other solvents.

The remaining material from the reaction mixture was next saponified by refluxing for 3 hours with 10% NaOH. Biphenyl was steam distilled from the alkaline solution, extracted into ether from the distillate, and determined quantitatively by optical density at 248 mμ in ethanol. Acids produced in the saponification were determined by acidifying the residue from the steam distillation, taking up into ether and separating as before.

The material finally remaining appeared to be chiefly a mixture of undefined and intractable tars which, in CO experiments, showed some infrared absorption in the carbonyl region. A 1.22-g. sample of this material (from 27.5 m*M* peroxide) was chromatographed on 25 g. of acid-washed alumina, using petroleum ether, benzene and ether as eluents. A yellow solid (110 mg.) was eluted by 1:1 petroleum ether–benzene. On two recrystallizations from aqueous ethanol it had m.p. 100.2–100.6° and a mixed m.p. with authentic *p*-phenylbenzophenone showed no depression.

Products from Cyclohexane Experiments.—Reaction mixtures obtained from CO experiments were again yellow and darker than controls. Acids and anhydrides were determined by diluting reaction mixtures to known volume with further cyclohexane and titrating two aliquots, one with 0.3 *N* sodium methoxide in methanol and the other with 0.5 *N* aqueous sodium hydroxide after adding 40 ml. of pyridine and 5 ml. of water and evaporating off most of the cyclohexane on a steam-bath. Thymol blue (0.4% in acetone) was used as the indicator.[33] Since anhydrides behave as monobasic acids in the first titration and dibasic acids in the second, both acid and anhydride may be determined. This method, which is relatively rapid, gave good agreement with the isolation procedure described previously. In one run, analyzed by both methods, yields of acid (moles/mole peroxide decomposed) were 0.73 (titration) 0.73 (hydrolysis) and of anhydride 0.32 (titration), 0.31 (hydrolysis). Esters were determined by saponifying another aliquot with 10% NaOH, separating and determining the acids as described previously, and deducting the known quantities of acid and anhydride. Benzene was determined on another aliquot by distilling to dryness and determining the optical density of the distillate at 255 mμ.

The composition of the acids, free and combined, was investigated as follows. Free acids were extracted with bicarbonate, converted to their methyl esters[34] and analyzed by gas chromatography using an Apiezon column at 130°. In control experiments the esters proved to be 25–33% methyl benzoate plus a mixture of much higher-boiling material, presumably methyl cyclohexylbenzoates.[19] In CO experiments the higher-boiling esters were absent, and the products were methyl benzoate plus variable amounts of methyl cyclohexanecarboxylate. A portion of the acid-free residue from the above separation was evaporated, taken up in benzene, and treated with aniline. The resulting precipitate on recrystallization proved to be benzanilide, m.p. 160–162°, mixed m.p. 161–163°, direct evidence for the presence of a benzoic anhydride. Hydrolysis of the remainder, with 0.109 *N* H_2SO_4, conversion of the acids to methyl esters and gas chromatographic analysis again showed them to be mixtures of benzoic and cyclohexanecarboxylic acids. The same acids (as methyl esters) were also detected by refluxing the remaining ester fraction with methanol and H_2SO_4, and carrying out gas chromatography on the steam-volatile fraction resulting.

Reaction mixtures from runs under CO containing traces of O_2 contained small amounts (under 100 mg.) of a white solid which could be separated by filtration and recrystallized from ethyl acetate, m.p. 281–285°. It gave a positive hydroxamic acid test for ester, but a negative one for anhydride.[35] *Anal.* showed C, 73.02, 73.09; H, 4.22, 4.3; mol. wt., 531. Calcd. for $C_{34}H_{22}O_8$ (the tetrabenzoate of 1,2,4,5-tetrahydroxybenzene): C, 73.11; H, 3.97; mol. wt., 559. A number of attempts were made to isolate further products from the CO experiments, but without significant success. Reaction mixtures gave negative tests for aldehyde and no carbonyl derivatives could be identified.

Products from Carbon Tetrachloride Experiments.—Runs under CO employed O_2-free gas, and were almost colorless. Reaction mixtures smelled strongly of benzoyl chloride and showed several carbonyl peaks at 5.6–6.0 μ. They were diluted to a known volume with additional CCl_4 and an aliquot slowly distilled off through a short fractionating column. Two additional portions of CCl_4 were added and the distillation continued. Benzene was determined from the optical density of the distillate at 262 mμ.

The fractionating column was next rinsed with ether. The rinsings and pot residue were evaporated and hydrolyzed by refluxing 3 hours with 5% aqueous NaOH. This alkaline solution was then extracted with ether for the determination of chlorobenzene and hexachloroethane described below. The basic layer was next acidified and extracted with ether. White insoluble terephthalic acid from the hydrolysis of *p*-trichloromethylbenzoic acid[36] separated at this point and was filtered off, dried and weighed. Ether-soluble acids were determined by bicarbonate extraction and identified as solely benzoic acid (gas chromatography of methyl esters) in the CO experiments. Only traces of ether-soluble acids were detected in controls. Another aliquot of the original solution was now titrated with 0.3 *N* sodium methoxide. Experiments on known blanks showed that both *p*-trichloromethylbenzoic acid and benzoyl chloride (like benzoic anhydride) titrate as monobasic acids with this reagent. Accordingly, since total organic acid residues and *p*-trichloromethylbenzoic acid had already been determined, the amounts of benzoic anhydride and benzoyl chloride could be calculated.

The ether solution mentioned above was next carefully evaporated under a short column, a weighed amount of anisole added to the viscous residue, and the whole (after dilution with a little CCl_4) subjected to gas chromatog-

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(33) D. M. Smith and W. M. D. Bryant, THIS JOURNAL, **58**, 2452 (1936).

(34) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 63.

(35) F. Feigl, "Spot Tests in Organic Analysis," 5th Ed., Elsevier Publishing Co., New York, N. Y., 1956, p. 237.

(36) J. Boeseken and H. Gelissen, *Rec. trav. chim.*, **43**, 869 (1924). This hydrolysis occurs very readily merely on extracting the original solution with cold 5% NaOH.

raphy at 150° on a diisodecyl phthalate column. Only ether, carbon tetrachloride, chlorobenzene, anisole and hexachloroethane were detected (in that order). Anisole served as an internal standard, and yields of chlorobenzene and hexachloroethane were calculated after calibration of the system with known mixtures.

The products of a CO experiment were further definitely identified as follows. After removal of most of the solvent, a reaction mixture was fractionally distilled at 17 mm. pressure. Chlorobenzene was first collected and identified by boiling point and infrared spectrum. As the temperature was raised a mixture of benzoyl chloride and sublimed hexachloroethane was collected. It was rinsed into a flask with ether and gently evaporated. The liquid portion had an infrared spectrum identical with authentic benzoyl chloride artificially contaminated with ether, and reacted exothermically with aniline to give benzanilide. Continued distillation of the residue at 0.09 mm. pressure gave a liquid, b.p. 122°, which solidified on standing. Its melting point on recrystallization was 39–42° (reported for benzoic anhydride, 42°) and its infrared spectrum was identical with authentic anhydride.

Experiments in Benzaldehyde.—A 0.1 *M* solution of benzoyl peroxide was decomposed in freshly distilled benzaldehyde at 70° under nitrogen, and the reaction followed by titration of aliquots (Fig. 1). After complete reaction the excess benzaldehyde was removed at 67° and reduced pressure, the residue dissolved in ether and extracted with $NaHSO_3$ solution to remove remaining aldehyde. The dibenzoate of dihydrobenzoin which separated from the ether solution and is a known product of the reaction[16] was removed and identified by m.p. (245.4–246.0°). A known aliquot of the ether solution was next extracted with bicarbonate and anhydride determined by hydrolysis as above. Further evidence for anhydride was obtained by extracting another aliquot with bicarbonate and examinating the infrared spectrum of the residue which showed strong peaks at 5.58 and 5.80 μ. Treatment of the residue with aniline and warming briefly yielded benzanilide, identified by m.p. and mixed m.p.

Deuterated benzoyl peroxide was prepared by treating toluene with two successive portions of D_3PO_4 (from D_2O and P_2O_5) for 88 hours at 80°. The deuteriotoluene was next oxidized to deuteriobenzoic acid with neutral $KMnO_4$, converted to the acid chloride with $SOCl_2$ and treated with a cold solution of Na_2O_2 (over-all yield 32%). A small scale run of the first step indicated 95% replacement of the ring protons by n.m.r. spectra, but the actual preparation used showed only 35–40%. Kinetic runs are shown in Fig. 2, and calculation indicates that, if deuteration were random, a value of $k_H/k_D = 1.5$ should give a 25-minute increase in half-life of the peroxide which should be readily apparent (actually, deuteration was probably selective in the *o*- and *p*-positions which would considerably increase the sensitivity of the experiment). As a further check, the n.m.r. spectra of benzoic acids prepared from (a) unused deuterated peroxide and (b) peroxide remaining after 73% reaction were compared. No significant difference (±5%) in deuterium content could be detected.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Equilibration of *cis*- and *trans*-Cycloalkenes[1]

BY ARTHUR C. COPE, PHYLIS T. MOORE[2] AND WILLIAM R. MOORE

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The *cis* and *trans* isomers of cyclononene, cyclodecene, cycloundecene and cyclododecene have been equilibrated in acetic acid solution at 79.9, 100.4 and 130.0°. The standard free energies, enthalpies and entropies of isomerization have been calculated at 100.4°. The equilibrium *cis*-olefin/*trans*-olefin ratios in acetic acid at 100.4° are cyclononene, 232; cyclodecene, 12.2; cycloundecene, 0.406; and cyclododecene, 0.517. Possible effects of the solvent on the positions of these equilibria are discussed. In the isomerization of *trans*-cyclononene, it was found that *cis*-cyclononene and cyclononyl acetate are formed at nearly equal rates; the concentration of the latter then slowly decreases as the system approaches equilibrium.

Our continuing interest in medium ring compounds has prompted a study of the equilibria between the *cis* and *trans* isomers of cyclononene, cyclodecene, cycloundecene and cyclododecene in acetic acid solution. No systematic study of these equilibria has been reported previously, although the greater stability of the *cis* relative to the *trans* isomer in the C_9- and C_{10}-rings has been recognized. Thus, *cis*-cyclononene essentially free of its *trans* isomer was obtained from *trans*-cyclononene that had been heated at 150° in the presence of β-naphthalenesulfonic acid.[3] Heating *trans*-cyclodecene in the presence of the same catalyst at 90–180° has resulted in substantial (70–80%)[4] to nearly complete[3] isomerization to *cis*-cyclodecene. Recently Allinger[5] has reported that treatment of either *cis*- or *trans*-cyclodecene with concentrated sulfuric acid at 25° gave *cis*-cyclodecene containing less than 0.5% of *trans*-cyclodecene (based on infrared analysis) and thus estimated that at equilibrium the *cis*/*trans* ratio was ≥ 200.[6]

Turner and Meador[7] have determined the heats of hydrogenation in acetic acid at 25° for *cis*- and *trans*-cyclooöctene, cyclononene and cyclodecene. The enthalpies of isomerization (*trans* to *cis*) calculated for the C_8-, C_9-, and C_{10}-olefins from their hydrogenation results are −9.2, −2.9 and −3.3 kcal./mole, respectively.

After the work described in this paper had been completed, Svoboda and Sicher[8] reported that the sulfuric acid-catalyzed equilibration of the cyclododecenes at room temperature gives a *cis*/*trans* ratio of about 40/60.

Preparation of Olefins.—*cis*-Cyclononene,[9,10] *cis*-cyclodecene[4,11] and *cis*-cycloundecene[12] were pre-

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(5) N. L. Allinger, *ibid.*, **79**, 3443 (1957).

(6) Dr. P. E. Fanta has informed us that in similar experiments he has found *ca.* 1% of the *trans* isomer (analysis by gas chromatography) indicating an equilibrium *cis*/*trans* ratio of *ca.* 100.

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