A Theoretical Study of the Elementary Steps Involved in the Reaction of Benzoyl Peroxide with Benzene[1-3]

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Abstract: Product and rate data for the thermal decomposition of benzoyl peroxide in benzene show that the reaction is complex. Mechanisms (consisting of the equations, plus the rate constants for each, plus the initial concentrations) based on several sets of 200–300 elementary steps have been evaluated quantitatively by computer techniques and the minor reactions eliminated on the basis of demonstrated unimportance. A resulting set of about 100 elementary steps has been shown to give good quantitative correlations between observed and calculated product yields as a function of peroxide concentration. Assignments of rate constants are discussed critically. The study provides a number of insights as to the extent to which the decomposition of benzoyl peroxide may be relied upon in mechanism studies involving free-radical intermediates. Application of the rate constants to the mechanism proposed by Hey and Perkins for the thermal decomposition of phenylazotriphenylmethyl accounts quantitatively for the once puzzling absence of dihydrobiphenyl and of tetrahydroquaterphenyl.

An understanding of the reaction steps for the thermal decomposition of benzoyl peroxide in benzene is fundamental to the effective use of peroxides as sources of aryl and aroyloxy radicals and to the study of the free-radical arylation process. Previous studies have, of necessity, focused on a few steps, for the difficulties of kinetic analysis quickly become formidable as steps are added.[4-12] The pioneering work of Nozaki and Bartlett[11] has formed the basis for many of the subsequent analyses of the kinetics.

We have used the computer program REMECH[13] to study a variety of plausible mechanisms. This approach requires assignment of a rate constant to each step in the mechanism. By combining information about product distribution from the thermal decomposition in several different solvents, the known absolute rate constants of representative free-radical reactions, the somewhat limited data on the kinetics of benzoyl peroxide reactions, and the recent detailed product studies of the thermal decomposition in benzene,[3,7-9] it is possible to assign plausible rate constants,

within a power of ten or so, to most of the key classes of reaction. There are about 15 of these classes.

The mechanism listed in Table I is representative of several which have been evaluated theoretically. Abbreviations are explained in Table II. Representative portions of the mechanism are shown in Figures 1 and 2. Although more than 50 reactants and products are included, of which about 20 are steady-state intermediates, this mechanism is a rather small sample of the complete system. To include all possible termination steps for 20 radicals requires more than 400 equations, allowing for both disproportionation and combination. Since a given abbreviation represents several position isomers as well as an even more numerous set of stereoisomers, it is obvious that thousands of equations would be required for a detailed description. Fortunately, certain reactions can be combined with little loss of generality and many other reactions are inconsequential. By investigating mechanisms which include a variety of representative steps even though some are presumably less plausible, there is a partial safeguard against the type of circular logic which discovers that a proposed series of steps is important primarily because other more important steps have been ignored. Rate constants were assigned on the basis of the reaction classes presented in Table III. The class number is shown in column 2 of Table I and in column 1 of Table III. A comparison of calculated and observed product distributions is given in Table V and is discussed later. See also Figures 1 and 2 of ref 3.

With the REMECH computer program it is possible to treat such complexity in quantitative terms. With hand calculation it is simply not feasible to include enough steps to account for the wealth of experimental detail.

To describe this complex system as clearly as possible, the next section presents a critical evaluation of the probable reaction rate for each class of reaction and an *a priori* value is assigned for each. In most cases there is an uncertainty of a factor of 10 or more, and the values actually used in Table I were chosen to give the best fit to the product distribution. The results are evaluated in the Results and Discussion which follow.

(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF AFOSR-62-279.

(2) We wish to acknowledge with appreciation the computing time made available by the Computing Center at Florida State University. Patrick Duncan and Victor M. Day helped with certain phases of the computations.

(3) D. F. DeTar, R. A. J. Long, J. Rendleman, J. Bradley, and P. Duncan, *J. Am. Chem. Soc.*, **89**, 4051 (1967).

(4) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 474.

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(7) E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Am. Chem. Soc.*, **82**, 2936 (1960).

(8) D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, 3412 (1964); D. I. Davies, D. H. Hey, and G. H. Williams, *ibid.*, 562 (1961).

(9) G. B. Gill and G. H. Williams, *ibid.*, 995, 7127 (1965); W. R. Foster and G. H. Williams, *ibid.*, 2862 (1962).

(10) (a) B. Barnett and W. E. Vaughan, *J. Phys. Chem.*, **51**, 926 (1947); (b) *ibid.*, **51**, 945 (1947).

(11) (a) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946); (b) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

(12) *Cf.* C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

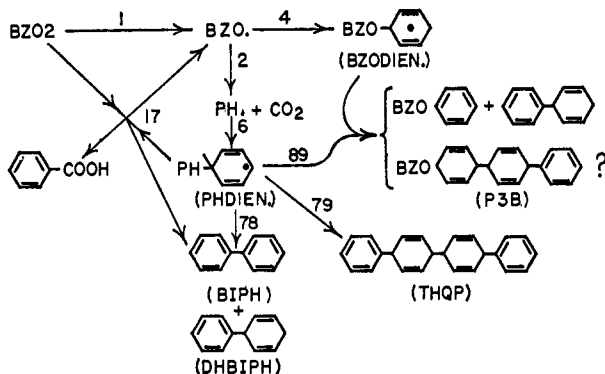(13) D. F. DeTar and C. E. DeTar, *J. Phys. Chem.*, **70**, 3842 (1966).

Figure 1. Primary reaction stages. Reaction numbers correspond to those in Table I. Abbreviations are those used in Tables I and II. For simplification only one isomer is shown though many are formed, and likewise only one direction of disproportionation is shown.

Figure 2. Representative secondary reactions. Caption notes to Figure 1 apply. The reaction labeled (*cf.* 66) was included in the 250-equation mechanism and found to be relatively negligible using the tabulated rate constants (Table I). Radicals labeled with the suffix L are allylic; so are THQP·, DHQP·, PHDIEN, and BZODIEN. The rest are alkyl, as shown for P3.

Identification of the Elementary Steps and Assignments of Class Rate Constants. Reaction Class 1 (4×10^{-5}).[14]

Evidence for this single-bond cleavage step was provided initially by trapping the benzoyloxy radicals with iodine and water; the rate was not affected by the iodine thus showing that iodine does not cause induced decomposition. With water also present, benzoic acid was formed in "quantitative" yield while in the absence of water the principal product was iodobenzene.[15] Many trapping agents reduce the carbon dioxide yield to 0.05 mole/mole of peroxide or less.[16]

There is some indication that multiple-bond cleavage or the carboxy inversion reaction[17] may play a minor role: (1) the carbon dioxide yields do not drop to zero, and (2) phenyl benzoate and biphenyl appear to be definite though minor "cage" products in cyclohexane.[18,19]

The rate of decomposition of benzoyl peroxide increases with increasing peroxide concentration and has been described in terms of a first-order term plus a higher-order term, either of the three-halves power[9,11] or of the second power (rate $= k_1P + k_iP^{3/2}$ or rate $= k_1P + k_2P^2$).[10,20] These terms have been identified with a primary decomposition, (reaction class 1) and with induced decomposition (*i.e.*, attack of radicals on the peroxide), but such assignments are far from certain since induced decomposition may give rise to first-order kinetics, or presumably anything between one-half and second-order kinetics.[11,12] The fact that the products become relatively simple in dilute solution lends some support to the above dissection. Gill and Williams report 1.88×10^{-5} for the value of k, obtained as an intercept by using iodometric determina-

(14) Reactions are identified by class as presented in Table III. The *a priori* estimates of the class rate constants are given in parentheses, while the values given in Tables I and III are those used to give the results reported in Tables V and VI. Units of all rate constants are 1. mole^{-1} sec^{-1}.

(15) (a) G. S. Hammond and L. M. Soffer, *J. Am. Chem. Soc.*, **72**, 4711 (1950); (b) G. S. Hammond, *ibid.*, **72**, 3737 (1950).

(16) D. F. DeTar and R. C. Lamb, *ibid.*, **81**, 122 (1959).

(17) J. E. Leffler, *ibid.*, **72**, 67 (1950).

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

(19) The argument is that decarboxylation of benzoyloxy radicals is too slow to compete with "cage" reactions, and that "cage" products involving phenyl radicals therefore require formation of phenyl radicals in the primary breakdown of the peroxide.

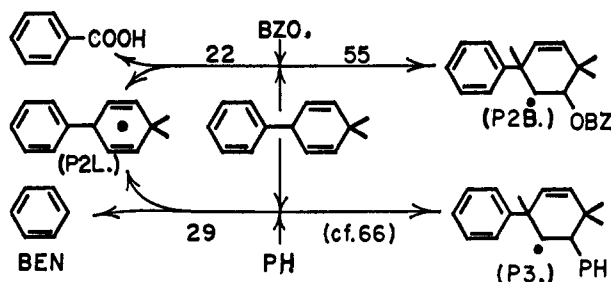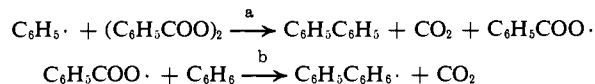(20) D. J. Brown, *J. Am. Chem. Soc.*, **62**, 2657 (1940).

tion of the peroxide, and 1.67×10^{-5} as the value in the presence of inhibitors.[9]

On the basis of the simple dissection, the data of Nozaki and Bartlett[11] indicate 15% induced decomposition at 0.01 M peroxide, the data of Gill and Williams about 17%, and the older data of Barnett and Vaughan about 8% if they are fitted to an equation of first plus three-halves order. The available kinetic data are summarized in Table IV.

For the present treatment the value used for k_0 is actually immaterial. The product distribution depends only on the other rate constants, and for these only the ratios are significant. The value used was 4×10^{-5}, corresponding to a temperature of about 87°.

Reaction Class 2 (1×10^4). This step is required for carbon dioxide formation. Alternatives are various types of induced decomposition such as the decarboxylative substitution steps a and b. Steps of this type have

$$C_6H_5 \cdot + (C_6H_5COO)_2 \xrightarrow{a} C_6H_5C_6H_5 + CO_2 + C_6H_5COO \cdot$$

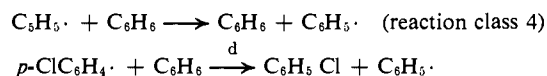$$C_6H_5COO \cdot + C_6H_6 \xrightarrow{b} C_6H_5C_6H_6 \cdot + CO_2$$

been seriously proposed, but there is no evidence requiring them. Reaction c, *e.g.*, can be excluded when R is alkyl since an optically active 1-phenyl-2-propyl group gives racemic 1-phenyl-2-chloropropane.[21] The

$$RCOO \cdot + CCl_4 \xrightarrow{c} RCl + CO_2 + \cdot CCl_3$$
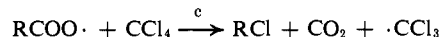
proper value of k_2 is unknown and a value of 10^4–10^5 sec^{-1} has been chosen so as to give the appropriate amount of CO_2.

Reaction Class 3 (2×10^3) and Reaction Class 4 (50). The origin of the various tetrahydroquaterphenyls and of the dihydrobiphenyls plus the biphenyl can all be most simply accounted for by postulating the formation of the phenylcyclohexadienyl radical. The experiments of Eliel with deuterated benzene demonstrate that the addition is not rapidly reversible.[7]

An order of magnitude estimate of k_3 (reaction class 3, Table III) is available from consideration of reaction class 4 and reaction d; $k_3/k_4 = 40$ and $k_4 = 50$. Therefore $k_3 = 2000$ 1. mole^{-1} sec^{-1}. The basis for these numbers is now described.

$$C_6H_5 \cdot + C_6H_6 \longrightarrow C_6H_6 + C_6H_5 \cdot \quad \text{(reaction class 4)}$$

$$p\text{-}ClC_6H_4 \cdot + C_6H_6 \xrightarrow{d} C_6H_5Cl + C_6H_5 \cdot$$

(21) The problem of decarboxylative substitution is discussed by D. F. DeTar and C. Weis, *ibid.*, **79**, 3045 (1957).

Table I. A Mechanism for the Thermal Decomposition of Benzoyl Peroxide in Benzene

Reactn no.	Class[a] no.	Elementary steps	Rate[a] const	Amount of reaction[b] 0.01	0.3
		Initial Steps			
1	A1	$BZO2 = BZO\cdot + BZO\cdot$	4×10^{-5}	96.6	79.6
2	A2	$BZO\cdot = PH\cdot + CO2$	1×10^4	181.5	130.0
3	A6	$BZO\cdot + C6H6 = BZOH + PHS\cdot$	10	2.0	1.4
4	A5	$BZO\cdot + C6H6 - BZODIEN\cdot$	35	7.0	4.9
5	A4	$PH\cdot + C6H6 = BEN + PHS\cdot$	50	4.4	2.9
6	A3	$PH\cdot + C6H6 = PHDIEN\cdot$	2×10^3	174.4	116.6
7	A3	$PHS\cdot + C6H6 = PHDIEN\cdot$	2×10^3	6.4	4.3
		Induced Decomposition Steps			
8	P27	$PH\cdot + BZO2 = PHBZOH + BZO\cdot$	500	0.0	0.5
9	P22	$PH\cdot + BZO2 = PHOBZ + BZO\cdot$	10	0.0	0.0
10	P25	$P2B\cdot + BZO2 = BIPH + BZOH + BZOH + BZO\cdot$	4×10^3	0.1	1.4
11	P26	$P2B\cdot + BZO2 = P2B2 + BZO\cdot$	100	0.0	0.0
12	P25	$P3B\cdot + BZO2 = P3B + BZOH + BZO\cdot$	4×10^3	0.0	0.3
13	P26	$P3B\cdot + BZO2 = P3B2 + BZO\cdot$	100	0.0	0.0
14	P25	$P4B\cdot + BZO2 = P4B + BZOH + BZO\cdot$	4×10^3	0.3	3.8
15	P25	$P2B2\cdot + BZO2 = P2B2 + BZOH + BZO\cdot$	4×10^3	0.0	0.5
16	P26	$P2B2\cdot + BZO2 = P2B + BZOH + BZOH + BZO\cdot$	100	0.0	0.0
17	P23	$PHDIEN\cdot + BZO2 = BIPH + BZOH + BZO\cdot$	10	2.6	9.8
18	P24	$PHDIEN\cdot + BZO2 = P2B + BZO\cdot$	1	0.3	1.0
19	P23	$THQP\cdot + BZO2 = DHQP + BZOH + BZO\cdot$	10	0.1	2.4
20	P24	$THQP\cdot + BZO2 = P4B + BZO\cdot$	1	0.0	0.2
21	P23	$DHQP\cdot + BZO2 = QP + BZOH + BZO\cdot$	10	0.0	0.6
		Hydrogen-Abstraction Reactions			
22	AB12	$DHBIPH + BZO\cdot = PHDIEN\cdot + BZOH$	2×10^4	0.5	2.8
23	AB12	$THQP + BZO\cdot = F2^c = THQP\cdot + BZOH$	2×10^4	1.7	5.1
24	AB12	$DHQP + BZO\cdot = DHQP\cdot + BZOH$	2×10^4	0.0	0.9
25	AB12	$P2B + BZO\cdot = P2BL\cdot + BZOH$	2×10^4	0.0	0.9
26	AB12	$P4B + BZO\cdot = P4BL\cdot + BZOH$	2×10^4	0.0	2.3
27	AB12	$P2B2 + BZO\cdot = P2B2L\cdot + BZOH$	2×10^4	0.0	0.3
28	AB12	$P4B2 + BZO\cdot = P4B2L\cdot + BZOH$	2×10^4	0.0	0.8
29	AB10	$DHBIPH + PH\cdot = PHDIEN\cdot + BEN$	5×10^4	0.5	2.9
30	AB10	$THQP + PH\cdot = F2 = THQP\cdot + BEN$	5×10^4	1.9	5.2
31	AB10	$DHQP + PH\cdot = DHQP\cdot + BEN$	5×10^4	0.0	1.0
32	AB16	$DHBIPH + P2B\cdot = P2B + PHDIEN\cdot$	2×10^4	0.1	0.6
33	AB16	$P2B + P2B\cdot = P2B + P2BL\cdot$	2×10^4	0.0	0.2
34	AB16	$P2B\cdot + DHBIPH = P2B + PHDIEN\cdot$	2×10^4	0.1	0.6
35	AB16	$P4B\cdot + DHBIPH = P4B + PHDIEN\cdot$	2×10^4	0.4	1.5
36	AB16	$P6B\cdot + DHBIPH = P6B + PHDIEN\cdot$	2×10^4	0.0	2.2
37	AB16	$P2B2\cdot + DHBIPH = P2B2 + PHDIEN\cdot$	2×10^4	0.0	0.3
38	AB16	$P3B2\cdot + DHBIPH = P3B2 + PHDIEN\cdot$	2×10^4	0.0	0.0
39	AB16	$P4B2\cdot + DHBIPH = P4B2 + PHDIEN\cdot$	2×10^4	0.0	1.1
40	AB16	$P2B\cdot + THQP = F2 = P2B + THQP\cdot$	2×10^4	0.4	1.0
41	AB16	$P4B\cdot + THQP = F2 = P4B + THQP\cdot$	2×10^4	1.6	2.6
42	AB16	$P6B\cdot + THQP = F2 = P6B + THQP\cdot$	2×10^4	0.1	3.4
43	AB16	$P2B2\cdot + THQP = F2 = P2B2 + THQP\cdot$	2×10^4	0.0	0.4
44	AB16	$P3B2\cdot + THQP = F2 = P3B2 + THQP\cdot$	2×10^4	0.0	0.0
45	AB16	$P4B2\cdot + THQP = F2 = P4B2 + THQP\cdot$	2×10^4	0.0	1.8
46	AB16	$P5B2\cdot + THQP = F2 = P5B2 + THQP\cdot$	2×10^4	0.0	0.0
47	AB16	$P2B\cdot + DHQP = P2B + DHQP\cdot$	2×10^4	0.0	0.2
48	AB16	$P4B\cdot + DHQP = P4B + DHQP\cdot$	2×10^4	0.0	0.5
49	AB16	$P6B\cdot + DHQP = P6B + DHQP\cdot$	2×10^4	0.0	0.8
50	AB16	$P2B2\cdot + DHQP = P2B2 + DHQP\cdot$	2×10^4	0.0	0.1
51	AB16	$P3B2\cdot + DHQP = P3B2 + DHQP\cdot$	2×10^4	0.0	0.0
52	AB16	$P4B2\cdot + DHQP = P4B2 + DHQP\cdot$	2×10^4	0.0	0.4
53	AB16	$P5B2\cdot + DHQP = P5B2 + DHQP\cdot$	2×10^4	0.0	0.0
54	AB16	$P6B2\cdot + THQP = F2 = P6B2 + THQP\cdot$	2×10^4	0.0	3.4
		Addition Steps			
55	AD11	$DHBIPH + BZO\cdot = P2B\cdot$	3×10^5	0.7	4.2
56	AD11	$P3 + BZO\cdot = P3B\cdot$	3×10^5	0.0	0.2
57	AD11	$THQP + BZO\cdot = F2 = P4B\cdot$	3×10^5	2.6	7.6
58	AD11	$DHQP + BZO\cdot = P4B\cdot$	3×10^5	0.0	1.4
59	AD11	$P6 + BZO\cdot = F3^c = P6B\cdot$	3×10^5	0.2	6.7
60	AD11	$P2B + BZO\cdot = P2B2\cdot$	3×10^5	0.0	1.3
61	AD11	$P3B + BZO\cdot = P3B2\cdot$	3×10^5	0.0	0.1
62	AD11	$P4B + BZO\cdot = P4B2\cdot$	3×10^5	0.0	3.5
63	AD11	$P5B + BZO\cdot = P5B2\cdot$	3×10^5	0.0	0.0
64	AD11	$P6B + BZO\cdot = F3 = P6B2\cdot$	3×10^5	0.0	3.7
65	AD3	$PH\cdot + BIPH = P3L\cdot$	2×10^3	0.0	0.5
66	AD9	$THQP + PH\cdot = F2 = P5\cdot$	5×10^3	0.2	0.5
67	AD9	$P2B + PH\cdot = P3B\cdot$	5×10^3	0.0	0.1

Table I (*Continued*)

Reactn no.	Class[a] no.	Elementary steps	Rate[a] const	Amount of reaction[b] 0.01	0.3
		Radical–Radical Reactions			
68	RR38	BZO· + PHDIEN· = BZOH + BIPH	5×10^7	0.1	0.3
69	RR39	BZO· + PHDIEN· = P2B	1×10^8	0.2	0.7
70	RR34	PH· + PHDIEN· = P3	1×10^8	0.1	0.3
71	RR45	P2B· + PHDIEN· = P4B	1×10^8	0.0	0.1
72	RR45	P4B· + PHDIEN· = P4B + BIPH	1×10^8	0.2	0.3
73	RR45	P4B· + PHDIEN· = P6B	1×10^8	0.2	0.3
74	RR45	P6B· + PHDIEN· = P8B	1×10^8	0.0	0.4
75	RR45	P3B2· + PHDIEN· = P5B2	1×10^8	0.0	0.0
76	RR45	P4B2· + PHDIEN· = P6B2	1×10^8	0.0	0.2
77	RR45	P6B2· + PHDIEN· = P8B2	1×10^8	0.0	0.3
78	RR42	PHDIEN· + PHDIEN· = BIPH + DHBIPH	4.5×10^6	25.1	14.1
79	RR43	PHDIEN· + PHDIEN· = THQP	1.05×10^7	58.5	32.9
80	RR42	DHQP· + PHDIEN· = QP + DHBIPH	4.5×10^6	0.0	1.0
81	RR43	DHQP· + PHDIEN· = P6	1.05×10^7	0.0	2.3
82	RR45	P5· + PHDIEN· = P7	1×10^8	0.2	0.5
83	RR45	P3B· + PHDIEN· = P5B	1×10^8	0.0	0.0
84	RR42	P4BL· + PHDIEN· = P4B + BIPH	4.5×10^6	0.0	2.3
85	RR42	P2B2L· + PHDIEN· = P2B2 + BIPH	4.5×10^6	0.0	0.3
86	RR42	P3L· + PHDIEN· = P3 + DHBIPH	4.5×10^6	0.0	0.5
87	RR42	THQP· + PHDIEN· = DHQP + DHBIPH	4.5×10^6	1.4	3.7
88	RR43	THQP· + PHDIEN· = P6	1×10^7	3.2	8.5
89	RR42	BZODIEN· + PHDIEN· = PHOBZ + DHBIPH	4.5×10^6	3.3	1.9
90	RR42	BZODIEN· + PHDIEN· = BEN + BZOH + BIPH	4.5×10^6	3.3	1.9
91	RR42	P2BL· + PHDIEN· = P2B + BIPH	4.5×10^6	0.0	0.2
92	RR42	P2BL· + PHDIEN· = P2B + DHBIPH	4.5×10^6	0.0	0.2
93	RR43	P2BL· + PHDIEN· = P4B	1.05×10^7	0.0	0.6
94	RR45	P2B2· + PHDIEN· = P4B2	1×10^8	0.0	0.0
95	RR42	P4B2L· + PHDIEN· = P4B2 + BIPH	4.5×10^6	0.0	0.8
96	RR37	BZO· + BZO· = BZO2	1×10^{10}	0.0	0.2
97	RR32	PH· + BZO· = PHOBZ	1×10^{10}	0.0	0.1
98	RR31	PH· + PH· = BIPH	1×10^{10}	0.0	0.0
99	RR43	THQP· + BZODIEN· = P5 + BZOH	1.05×10^7	0.4	1.1
100	RR42	THQP· + THQP· = DHQP + THQP	4.5×10^6	0.1	1.1
101	RR43	THQP· + THQP· = P8	1.05×10^7	0.2	2.4

[a] See Table III for class assignments. Units are l. mole^{-1} sec^{-1}. [b] Total reaction flux in moles $\times$ 100/mole of peroxide. This varies with extent of reaction and with initial peroxide concentration. Values are reported for 90% of reaction at initial benzoyl peroxide concentrations of 0.01 and 0.3 M. Initial benzene concentration was taken as 11 M. [c] F2 is a statistical factor of 2, F3 is a statistical factor of 3.

Reaction class 4 can be observed only if one ring is isotopically labeled,[7] while the related reaction d can be measured because of the substituent label. Reaction of *p*-chlorobenzoyl peroxide with benzene gives chlorobenzene and small amounts of biphenyl and dihydrobiphenyl as well as the expected *p*-chlorobiphenyl and *p*-chlorodihydrobiphenyl.[3] The formation of chlorobenzene shows that chlorophenyl radicals are abstracting hydrogen atoms from some substrate. This might be by reaction d or by abstraction from peroxide, from reaction products, or from other radicals. Peroxide is not a reasonable choice, for there should not be a great difference in reactivity of the hydrogen atoms of the solvent and of the peroxide and the solvent is presented in a 1000-fold excess. Reaction with the products is thought the most important source. Hydrogen abstraction by radical–radical reactions is not likely (see Results and Discussion).

Although the formation of chlorobenzene is inconclusive, the formation of biphenyl and dihydrobiphenyl in the decomposition of *p*-chlorobenzoyl peroxide in benzene suggests that phenyl radicals are produced. The only radicals reactive enough to abstract hydrogen atoms from benzene are chlorophenyl radicals and *p*-chlorobenzoyloxy radicals. Phenylcyclohexadienyl radicals are stabilized by resonance and should be even less reactive than styryl radicals.[22]

(22) Styryl radicals and allyl radicals are comparable in reactivity, and phenylcyclohexadienyl radicals have a more extended conjugated

The dideuteriobiphenyls formed in the reaction of benzoyl peroxide with monodeuteriobenzene may be attributed to hydrogen abstraction from the deuteriobenzene by phenyl radicals or benzoyloxy radicals followed by reaction of the deuteriophenyl radical with deuteriobenzene. Eliel discusses this and alternative mechanisms.[7]

The approximate ratio of unsubstituted biphenyl and dihydrobiphenyl to the chlorinated derivatives is

system than allyl radicals. Data are available for estimating the relative effectiveness of methyl radicals and styryl radicals in abstracting hydrogen atoms. The rate of the reaction of methyl radicals with benzene is reported[23] to be 1000 l. mole^{-1} sec^{-1} at 182°. From the reported

$$CH_3 \cdot + C_6H_6 \longrightarrow CH_4 + C_6H_5 \cdot$$
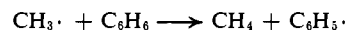
activation energy of 9.2 kcal/mole, the rate at 80° would be 50 l. mole^{-1} sec^{-1}. The rate of the corresponding reaction with styryl radicals may be estimated from chain-transfer constants (1.8 $\times$ 10^{-6})[24] and from the absolute rate constant for the propagation step (176).[25] This gives the value 3.2 $\times$ 10^{-4} at 60° or about 12 $\times$ 10^{-4} mole l.$^{-1}$ sec^{-1} at 80°. Actually there is considerable uncertainty about the details of the chain-

$$S_xCH_2\dot{C}HCH_6H_5 + C_6H_6 \longrightarrow S_xCH_2C_6H_5 + C_6H_5 \cdot$$
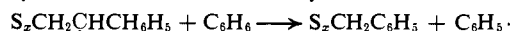
transfer reactions, and a different type of mechanism must be invoked for bromobenzene.[26] The above value is therefore a maximum one. The minimum ratio of the reactivities of methyl radicals and of styryl radicals toward hydrogen abstraction from benzene is therefore of the order of 40,000.
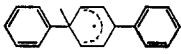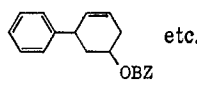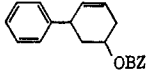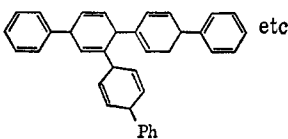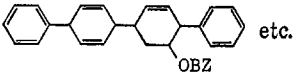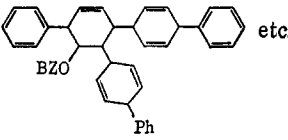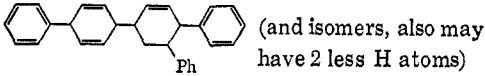
(23) A. F. Trotman-Dickenson, *Quart. Rev.* (London), 7, 198 (1953); J. M. Tedlen, *ibid.*, 14, 336 (1960).

(24) R. A. Gregg and F. R. Mayo, *Discussions Faraday Soc.*, 2, 328 (1947).

(25) M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, 73, 1700 (1951).

(26) F. R. Mayo, *ibid.*, 75, 6133 (1953).

Table II. Typical Reactants and Products Corresponding to Abbreviations in Table I[a]

BEN	Peroxide-derived benzene
BIPH	Biphenyl
BZO2	Benzoyl peroxide
C6H6	Solvent benzene
DHBIPH	Dihydrobiphenyl
DHQP	Dihydroquaterphenyl
PHBZOH	4-Phenylbenzoic acid (and isomers)

PH·	C_6H_5· (from peroxide)
BZO·	C_6H_5COO·
PHS·	C_6H_5· (from solvent)
PHDIEN·	$C_6H_5C_6H_6$·
BZODIEN	$C_6H_5COOC_6H_6$·

P3L·[b]

P2B

P3   Terphenyls and dihydroterphenyls

P4B   etc.

P5   (and isomers, also may have 2 less H atoms)

P2B·   etc.   OBZ

P6   etc.   Ph

P6B   etc.   BZO   Ph

[a] Abbreviations represent the sum of all position and stereoisomers. In some cases such as P4B they also represent different levels of hydrogenation. [b] Four types of radical are distinguished: aryl (such as phenyl), benzoyloxy, alkyl (P2B·), and allylic (PHDIEN· and radicals with an L suffix such as P3L·). These types were assigned separate rate constants as shown in Table III.

25:1000.[3] Assuming that reaction d (cf. reaction class 4) is responsible and that there is no discrimination in coupling, the ratio of rate constants k_3 and k_4 is therefore about 40. To the extent that reaction class 12 is involved this will be an underestimate.

Since the bond dissociation energy of the C–H bond of benzene is about the same as that for a C–H bond in methane,[4,23] the reactivity of the methyl radical and the phenyl radical in hydrogen abstraction should be comparable. This gives $k_4 = 50$ l. mole^{-1} sec^{-1}. MacLachlan and McCarthy estimate the rate constant for reaction class 3 to be 4.8×10^4 from pulse radiolysis.[27] This estimate is, however, coupled to an estimate of the rate of radical combination which is believed to be incorrect (see reaction classes 31–47).

Reaction class 5 (50) is the counterpart of reaction class 3. It appears to be the most likely step leading to phenyl benzoate[3,8] (see reaction class 22 for the reasons). The rate constant k_5 was therefore chosen so as to predict correctly the yield of phenyl benzoate.

Reaction class 6 and step e (10) (reaction 4) are a probable source of some phenyl radicals. An alkoxy radical

$$p\text{-}ClC_6H_4COO· + C_6H_6 \xrightarrow{e} p\text{-}ClC_6H_4COOH + C_6H_5·$$
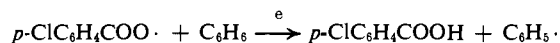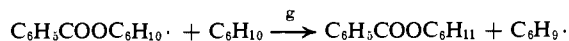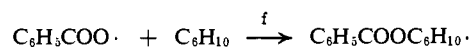
would be expected to abstract hydrogen atoms much faster than a carbon radical as judged by the high bond dissociation energy for the O–H bond, but the benzoate radical is resonance stabilized. The rate was therefore set in the same range as reaction class 5.

Reaction Class 9 (1 × 10⁴). The rate of addition of a phenyl radical to a double bond should be greater than rate of addition to a benzene ring (reaction class 3). Because of the high reactivity expected for a phenyl radical, the factor should not be more than about 100.

Reaction Class 10 (5 × 10⁴). Hydrogen abstraction from a doubly allylic position from such substrates as dihydrobiphenyl and tetrahydroquaterphenyl should be about 100–1000 times faster than abstraction from a

benzene ring (reaction class 4) judging from the results with methyl radicals.[23]

Reaction Class 11 (1 × 10⁴). In cyclohexene the major reaction product is cyclohexyl benzoate.[28,29] The mechanism has been postulated to involve reactions f and g. It may also be mentioned here that the reaction rate shows that there is little induced decomposition of the peroxide;[11] hence cyclohexenyl radicals do not readily attack peroxide.

$$C_6H_5COO· + C_6H_{10} \xrightarrow{f} C_6H_5COOC_6H_{10}·$$

$$C_6H_5COOC_6H_{10}· + C_6H_{10} \xrightarrow{g} C_6H_5COOC_6H_{11} + C_6H_9·$$

As the principal high molecular weight by-products are esters,[3] benzoyloxy radical addition to dihydrobiphenyl and to the tetrahydroquaterphenyls must be fast. Finally, the ratio of decarboxylation (reaction class 2) to addition to various monomers has ranged from 0.3 to 8.[30] The rate constant for reaction class 11 should therefore be roughtly 1–10 times the rate of reaction class 2.

Reaction Class 12 (1 × 10⁴). The arguments about rate estimates for abstraction of allylic hydrogen atoms by benzoyloxy radicals parallel those given for phenyl radicals (reaction class 10; see also reaction class 6). The rate for reaction class 12 is presumed to be at least 100–1000 times that of reaction class 6. It may be noted here that reaction classes 10, 12, and 16 must be those most directly involved in converting tetrahydroquaterphenyl to quarterphenyl. Since the yield of the p,p'-quaterphenyl approaches 1.5% in solutions initially 0.2 M in benzoyl peroxide, it must be surmised that the yield of the more soluble o,p'-quaterphenyl is comparable (since the two quaterphenyl position isomers are present in comparable amounts as the tetrahydro derivatives). One is thus forced to use the upper-limit

(27) A. MacLachlan and R. L. McCarthy, *J. Am. Chem. Soc.*, **84,** 2519 (1962).

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

(29) W. von E. Doering, K. Okamoto, and H. Krauch, *J. Am. Chem. Soc.*, **82,** 3579 (1960).

(30) Work of J. C. Bevington, summarized in his book, "Radical Polymerization," Academic Press Inc., London, 1961, p 43.

Table III. Summary of Reaction Classes

Class[a]	Reaction	Rate const
01	Initial cleavage of peroxide, BZO2 = BZO· + BZO·	4×10^{-5}
02	Decarboxylation step, BZO· = PH· + CO2	1×10^4
	Reactions with Aromatic Ring	
03	Phenyl addition to ring, PH· + C6H6 = PHDIEN·	2×10^3
04	Identity reaction, PH· + C6H6 = BEN + PH·	50
05	Benzoyloxy addition to ring, BZO· + C6H6 = BZODIEN·	35
06	H abstraction from ring by benzoyloxy, = BZOH + PH·	10
	Reactions with —C=C—CH—	
09	Phenyl addition to double bond	5×10^3
10	H abstraction by phenyl	5×10^4
11	Benzoyloxy addition to double bond	3×10^4
12	H abstraction by benzoyloxy[b]	2×10^4
13	Allyl addition to double bond	0.1
14	H abstraction by allyl	0.1
15	Alkyl addition to double bond	1
16	H abstraction by alkyl[b]	2×10^4
Induced Decomposition Steps, Radical Attack on Peroxide		
22	Phenyl, ester produced	10
23	Allyl, acid produced	10
24	Allyl, ester produced	1
25	Alkyl, acid produced	4×10^3
26	Alkyl, ester produced	100
27	Ring attack by phenyl	500
	Radical–Radical Reactions	
31	Phenyl–phenyl combination	1×10^{10}
32	Phenyl–benzoyloxy combination	1×10^{10}
33	Phenyl–allyl disproportionation	5×10^7
34	Phenyl–allyl combination	1×10^8
35	Phenyl–alkyl disproportionation	5×10^7
36	Phenyl–alkyl combination	1×10^8
37	Benzoyloxy–benzoyloxy combination	1×10^{10}
38	Benzoyloxy–allyl disproportionation	5×10^7
39	Benzoyloxy–allyl combination	1×10^8
40	Benzoyloxy–alkyl disproportionation	5×10^7
41	Benzoyloxy–alkyl combination	1×10^8
42	Allyl–allyl disproportionation	4.5×10^6
43	Allyl–allyl combination	10.5×10^6
44	Allyl–alkyl disproportionation	5×10^7
45	Allyl–alkyl combination	1×10^8
46	Alkyl–alkyl disproportionation	5×10^7
47	Alkyl–alkyl combination	1×10^8

[a] The numbers in the Class column correspond to the class number in Table I, column 2. [b] Only abstraction from allylic positions is included in the present treatment

estimates for the rate constants for these hydrogen-abstraction reactions.

Reaction Class 13 (0.1) and Reaction Class 14 (0.1). The rates of hydrogen abstraction and of addition by the allylic radicals is presumed to be negligible. The reactions were temporarily included to permit checking. The given rate constants are arbitrary.

Reaction Class 15 (1). From polymerization and copolymerization studies it is known that 1,2-disubstituted olefins are not very reactive toward alkyl radicals[31] (see Table III for examples of the alkyl radicals involved here). Furthermore the product studies show clearly that the resin fraction has few

(31) Reference 4, pp 118, 123.

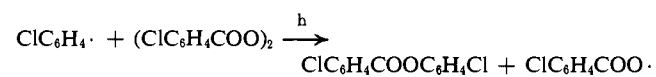**Table IV.** Rate of Decomposition of Benzoyl Peroxide in Benzene at 80°

Concn, $M \times 10^3$	$k_{obsd} \times 10^5$, sec^{-1}	$k_1{}^a \times 10^5$	Ref
3	2.2[b]		g
10	4.2	4.39,[c] 3.84[d]	10
10	2.3		9
11	3.0[e]		12
21	4.4		10
21	3.7	3.28[d]	11
22	2.4		9
50	4.3		12
25	3.3		h
25	2.7		20
43	2.6		9
86	3.0		9
100	4.7[f]		i
128	3.2		9
217	3.6		9

[a] The recent results of Gill and Williams[9] give $k_1 = 1.88 \times 10^{-5}$ and $k_{3/2} = 3.74 \times 10^{-5}$. [b] 1.2 at 75.8°. [c] Assuming first plus second order.[10] [d] Assuming first plus three-halves order, using $k_{obsd} = 0.1358 + 0.1211P^{1/2}$. [e] 2.6 at 79°. [f] 3.8 at 78°, corrected to 80° using $E = 32$ kcal. [g] C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951). [h] P. F. Hartman, H. G. Sellers, aud D. Turnbull, *J. Am. Chem. Soc.*, **69**, 2416 (1947). [i] J. H. McClure, R. E. Robertson, and A. C. Cuthertson, *Can. J. Chem.*, **20B**, 103 (1942).

components with more than about ten rings. It can therefore be concluded that polymerization is unimportant, and the rate constant 1 was arbitrarily assigned. However, this step may be required in order to allow simultaneously enough induced decomposition by reaction classes 24 and 26 and a residue of a high enough molecular weight.

Reaction Class 16 (1000). A secondary radical may be expected to be about 0.1 to 0.01 as reactive as a methyl or a phenyl radical. The upper limit was chosen for reasons summarized under reaction class 12.

Reaction Class 22 (10). Induced decomposition of benzoyl peroxide was once postulated as the source of the phenyl benzoate.[10] An analogy is the chain

$$\text{ClC}_6\text{H}_4\cdot + (\text{ClC}_6\text{H}_4\text{COO})_2 \xrightarrow{\text{h}}$$
$$\text{ClC}_6\text{H}_4\text{COOC}_6\text{H}_4\text{Cl} + \text{ClC}_6\text{H}_4\text{COO}\cdot$$

reaction of benzoyl peroxide with diethyl ether which requires attack of the peroxide by α-ethoxyethyl radicals to give α-ethoxyethyl benzoate.[32] It is, nevertheless, now clear that phenyl benzoate is not formed appreciably by reaction class 22.[3,8] Thus the major ester formed on decomposition of p-chlorobenzoyl peroxide in benzene is the monochloro ester, phenyl p-chlorobenzoate, and not the dichloro ester predicted by reaction h.[3] Another argument against reaction class 22 is that the yield of phenyl benzoate would increase markedly with concentration since this represents an induced decomposition step. The yield is actually almost constant at 3–4%.[3]

Reaction Class 23 (10), Reaction Class 24 (10), Reaction Class 25 (1 × 10³), and Reaction Class 26 (1 × 10³). Induced decomposition of benzoyl peroxide is of some importance in the reaction in benzene. It is clearly of great importance in ethers[11,32] and of moderate importance in cyclohexane.[11] This appears to be beyond the probable solvent effect. Both the

(32) W. E. Cass, *J. Am. Chem. Soc.*, **68**, 1976 (1946).

first-order term and the arbitrary three-halves-order term are especially large in cyclohexane. Taking the three-halves-order term literally, $k = 30 \times 10^{-5} = k_{induced}(k_t/k_1)^{1/2}$. (The definition of k_i is that employed by Nozaki and Bartlett.[11]) Taking k_t (reaction classes $46 + 47$) as about 10^8 and $k_1 = 4 \times 10^{-5}$, $k_{induced} = 500$. This is an underestimate since the first-order term also must concern induced decomposition.

Certain radicals are inefficient in giving induced decomposition of peroxide. Styrenes, e.g., serve as inhibitors of induced decomposition,[12,18] and this means that attack on peroxide by styryl radicals must be rather slow. The above-mentioned lack of induced decomposition in cyclohexene suggests that cyclohexenyl radicals are unreactive, and by the same token allyl radicals in the benzene system might be unreactive (see reaction class 11 for discussion). Reaction class 24 was assigned an arbitrarily small rate constant to be in accord with these conclusions.

Reaction class 23 (reaction 17, Table I) has been postulated as a reaction step to account for induced decomposition.[33] We therefore studied variations of the rate constants to establish the likelihood of this step. This reaction is special in that loss of a hydrogen atom gives an aromatic ring, and it might have a higher rate constant than the radical reactions mentioned above.

Reaction Class 27 (500). p-Phenylbenzoic acid is formed to some extent in relatively concentrated peroxide solution.[8,34] Walling has suggested a good mechanism for the reaction.[35] It may be noted that the principal acidic product is always benzoic acid, and therefore reaction class 27 is insignificant in dilute solution due to the low concentration of reactants.

The value of k_{27} was assigned so that there was formed 0.5% of p-phenylbenzoic acid in $0.2\ M$ peroxide solutions. In cyclohexane considerable cyclohexylbenzoic acid is formed,[28,35] but the observed neutral equivalent of the isolated acid fraction precludes more than traces of such a product here.[3]

Radical–Radical Reactions 31–47. The various possible radical–radical reactions have been reduced to 17 types as a workable compromise between the impossibility of individual rate assignments to each of several hundred reactions and assignment of a single rate for all. Absolute rate constants are available for several alkyl radicals in the gas phase[36] and for a number of polymer systems in solutions.[37] Values are not available for any of the reaction classes 31–47. As a starting point reations of phenyl radicals and of benzoyloxy radicals among themselves (reaction classes 31, 32, and 37) were assigned the rate constants of 1×10^{10} comparable to the gas-phase methyl radical rate. The other extreme is represented by the allyl radicals such as the phenylcyclohexadienyl radical. These reaction classes (42 and 43) were assigned rate con-

stants in the $10^6–10^7$ range on the assumption that they are roughly analogous to styryl radicals. Alkyl radical reaction classes (46 and 47) were assigned values of $10^7–10^8$ on the estimate that they would be 10–100 times as reactive as the allylic radicals. The cross-radical reaction might be assigned a geometric mean value or higher. There is evidence in some systems that cross-termination is favored over simple termination.[38]

In a very interesting study MacLachlan and McCarthy calculate a rate constant of 3×10^8 to 7×10^9 for processes in various aromatic solvents comparable to reaction classes 42 and 47. The work involved pulse radiolysis of aromatic solvents and direct observation of transient species by ultraviolet absorption.[27] Calculation of a second-order rate constant required estimations of concentrations which cannot be directly observed. In view of the 100–1000-fold discrepancy between these values and other known values for radical combination reactions, we question whether the elements of this complex system have been correctly identified.

Some statistical corrections have been included where consistency could be served. However, the uncertainty in the rate constants often makes such questions relatively pointless, and furthermore many of the rate constants are being applied rigidly to a very large set of reactions which will certainly show some variation in rates among themselves as well as variations in statistical factors. Attention was paid to adjusting ratios of combination and disproportionation.

Primary alkyl radicals react predominately by coupling, and so do styryl radicals; t-alkyl radicals are disproportionate.[39] Interaction of an alkyl radical and an acyloxy radical leads to both combination and disproportionation.[40]

The combination and disproportionation of phenylcyclohexadienyl radicals, reactions 44 and 45, represent major reaction steps in the decomposition of benzoyl peroxide in benzene. The ratio of combination to disproportionation is about 2. Combination yields in principle three position isomers, o,o'-, o,p'-, and p,p'-tetrahydroquaterphenyls. In addition there are six stereoisomers of the o,o' and six of the p,p' form and eight of the o,p' form. One of the 1',4',1'',4''-tetrahydro-p,p'-tetrahydroquaterphenyls separates in crystalline form, but a considerable portion of the p,p'-tetrahydroquaterphenyl fraction fails to crystallize. Beyond this suggestion there is little information on the stereoisomerism.

Hydrogenation studies give the ratio of o,o':o,p': p,p' as about $2.3:44:53$.[3] The statistical ratios would be $4:4:1$, and the most likely explanation is steric interference which discriminates against the ortho positions. Since no single ortho–para discrimination factor can give the observed product distribution, it is necessary to propose that there is a greater barrier to o,o' union than might be judged from the ratio of o,p' to p,p' isomers. This type of cumulative effect is common in cases of steric interactions.

(33) K. H. Pausacker, *Australian J. Chem.*, 10, 49 (1957).
(34) H. Gelissen and P. H. Hermans, *Ber.*, 58, 476 (1925).
(35) C. Walling and E. S. Savas, *J. Am. Chem. Soc.*, 82, 1738 (1960).
(36) In units of l. mole^{-1} sec^{-1}; the rate constant for methyl radicals is 2×10^{10} [A. Shepp, *J. Chem. Phys.*, 24, 939 (1956)]; for isopropyl radicals, 1×10^{11} [E. L. Metcalfe and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4620 (1962)]; for t-butyl radicals, 3×10^9 [E. L. Metcalfe, *ibid.*, 3560 (1963)].
(37) Reference 4, p 95. The "chemical" rates for such monomers as methyl methacrylate are probably of the order of $10^8–10^9$, and the observed rates are diffusion controlled: S. W. Benson and A. M. North, *J. Am. Chem. Soc.*, 84, 935 (1962), and references cited therein.

(38) Reference 4, p 146.
(39) (a) S. J. Lapporte, *Angew. Chem.*, 72, 759 (1960); (b) A. F. Trotman-Dickenson, *Ann. Rept. Progr. Chem.* (Chem. Sec. London), 50, 36 (1958); R. N. Birrell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4218 (1960).
(40) D. F. DeTar and D. V. Wells, *J. Am. Chem. Soc.*, 82, 5839 (1960).

Table V. Product Yields Predicted by Mechanism of Table I[a]

	Initial peroxide concn									
	0.001		0.01		0.1		0.3 (10%)	0.3 (90%)		1.0
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Calcd	Obsd	Calcd
CO_2	189	192	181	178	151	150	155	130	135	111
Benzoic acid	7	5	11	8	27	28	32	38	35	53
Biphenyl	32	...	31	38	29	36	38	31	35	36
Dihydrobiphenyl	31	...	27	18	13	5	19	5	3	1
Phenyl benzoate	3.6	4.1	3.3	3.5	2.4	2.9	2.9	2.0	2.7	1.8
Tetrahydroquaterphenyl	62	70	50	51	13	19	30	3	9	1
Dihydroquaterphenyl	0.2	...	1.5	...	3.6	...	2.7	1.9	...	0.4
Quaterphenyl	0	...	0	...	0.6	...	0.1	1.6	1[b]	2.3
Terphenyl	0	...	0.1	...	0.3	...	0.6	0.5	1[b]	0.8
Phenylbenzoic acid	0	0	0	...	0.2	...	0.9	0.5	1[b]	1.3
Benzene (peroxide derived)	8	...	10	...	14	...	11	14	...	11
Hydrocarbons C_{30}–C_{60}	1	...	11	...	34	...	15	28	...	14
Esters C_{19}–C_{62} (phenyl)	0.8	...	6	...	33	...	16	45[c]	38[d]	45[e]
(benzoyloxy)	0.5	...	5	...	18	...	10	29	22[d]	35[e]

[a] Entries are 100 × moles of incorporated phenyl or benzoyloxy radicals/mole of peroxide. Except as noted the observed values are from Table I of ref 3. [b] From Table II of ref 3 for 0.2 M peroxide. [c] Average molecular weight 522 excluding the C_{19} ester. [d] From Table III of ref 3 for 0.2 M peroxide. The 82 g of residue/mole of peroxide (0.2 M) is assumed to be 80% 3 and 20% 4 (ref 3). The three solvent derived rings are not counted. [e] Average molecular weight 705 excluding the C_{19} ester.

Table VI. Summary of Reaction Flow[a]

Reaction		Initial peroxide concn			
		0.01 (10%)	0.01 (90%)	0.3 (10%)	0.3 (90%)
Peroxide	Direct decompn	95	96	76	80
	Induced decompn	5	4	24	20
C_6H_5COO →	C_6H_5 + CO_2	185	181	155	130
	→ BzOH (abstr from C_6H_6)	2	2	2	1
	→ BzOH (abstr allylic H)	0.3	2	4	13
	→ Addn to C_6H_6	7	7	6	5
	→ Addn to C=C	0.4	3.6	7	29
	→ Radical–radical	0.4	0.3	2.4	1.3
C_6H_5	→ Addn to C_6H_6	180	174	144	116
	→ Addn to C=C	0	0.2	0.3	0.6
	→ C_6H_6 (abstr from C_6H_6)	4	4	4	3
	→ C_6H_6 (abstr allylic H)	0.3	2.4	4	9
	→ Radical–radical	0.1	0.3	0.7	0.4
$C_6H_5C_6H_6$ →	Biphenyl + dihydrobiphenyl	26	25	18	14
	→ Tetrahydroquaterphenyl	61	58	42	33
	→ Other radical–radical	8	14	15	27
	→ Oxidation by Bz_2O_2	4	3	15	10

[a] Expressed as mole % (moles of reaction × 100/moles of peroxide). Entries are for 0.01 and 0.3 mole of peroxide at 10 and 90% reaction.

The ratio of 1,2-dihydrobiphenyl to 1,4-dihydrobiphenyl is of the order of one-tenth. This may also result in part from a steric effect in the disproportionation reactions.

These details were not incorporated in the mechanism in Table I since they do not affect the kinetic results in a useful way at the present level of approximation.

Results and Discussion

One over-all aim of the study of reaction mechanisms is to provide a dictionary of elementary steps of the type shown in Table I. For each of these steps the rate constant is to be known as a function of temperature and environment. With such a dictionary it would be possible in principle to predict the outcome of any reaction providing information about all relevant steps which were included.

At present this approach can be applied only crudely, but the results of the attempt are nevertheless of interest, and they point the direction for future work. The rate constants of the reaction classes as presented in the preceding section have been taken as the relevant por-

tion of the dictionary. Some departures are to be expected since the estimates of the rate constants are crude, but a requirement for gross departures points to an area that needs further experimentation to see whether it is the rate constant or the mechanism that is wrong.

It was rather surprising to find that the range of rate constants which will account for the product distribution is narrowly circumscribed. However, with this complex system many compensations exist, and an increase of certain values may be accommodated by a precisely determined change in others. The rate constants in Table I are therefore not uniquely determined. The mechanism (Table I) may now be examined critically for the extent to which it accounts for all known results.

The over-all evaluation of the mechanism is that it accounts very well for most of the reaction products. This is shown in Table V. The reaction flow is summarized in Table VI. There are two unresolved discrepancies. First, it is not possible to reproduce the 18:38 ratio of dihydrobiphenyl to biphenyl in the 0.01 M run and simultaneously to get a good fit in the con-

centrated runs. Second, the predicted amount of induced decomposition is too low, and it appears that steps other than those shown in reactions 8–21 may have to be introduced. These will be considered in turn.

The problem of the dihydrobiphenyl–biphenyl ratio is that the calculated ratio of 27:32 (the total yield of C_{12} hydrocarbon is roughly the same as is observed) can be decreased by only three processes unless additional reactions are included in the mechanism: (1) oxidation of phenylcyclohexadienyl radicals, (2) oxidation of dihydrobiphenyl, or (3) selective loss of dihydrobiphenyl by addition reactions. The available oxidizing agents are (a) benzoyl peroxide, (b) benzoyloxy radicals, (c) phenyl radicals, and (d) alkyl radicals. Oxidation by a or b requires a corresponding increase in the benzoic acid yield, and this is already too high. The rate constant used for abstraction by alkyl radicals is already at an upper limit. Furthermore sufficient increases in the rates of any of the processes 1–3 to give the 18:38 ratio results in poor correlation in more concentrated runs.

We therefore tentatively conclude that the experimental dihydrobiphenyl yields may be low and suggest that the presence of small amounts of oxygen in the reaction may be the cause. The quantity of oxygen needed is about 0.02 mole/mole of peroxide, or about 20 ml for 4 l. of 0.01 M solution, and such an amount could perhaps come from incomplete outgassing.

It may be noted that product distributions change dramatically with initial peroxide concentration and also with the extent of reaction. This change occurs since many products are secondary or tertiary, formed, e.g., by addition of benzoyloxy radicals to primary products.

Certain yields can readily be touched up. The quaterphenyl yield is about right based on isolation of 1% of p,p'-quaterphenyl and on the expectation that a roughly equal amount of o,p'-quaterphenyl would be present since p,p'- and o,p'-tetrahydroquaterphenyl are both formed. The yield of terphenyls could be increased by assigning a somewhat larger rate constant for the phenylation of biphenyl, reaction 65. The phenyl benzoate yield can be increased by either increasing the rate of addition of benzoyloxy radicals to benzene (reaction 4) or by changing the disproportionation ratio (reactions 89 and 90).

The yields of high molecular weight esters are about as expected. The average molecular weights could be increased by adding further steps leading to larger molecules.

The amount of induced decomposition is low, 20% in 0.3 M solution. The major type of induced decomposition incorporated into the chosen set of rate constants is oxidation of phenylcyclohexadienyl radicals (reactions 17, 19, and 21). Another important contributor which has not been seriously considered before is removal of a hydrogen atom from substituted cyclohexyl radicals (reactions 12, 14, and 15). In cyclohexane the appreciable induced decomposition by cyclohexyl radicals leads in part to cyclohexylbenzoic acids but not appreciably to cyclohexyl benzoate.[35] It is probable that oxidation to cyclohexene is an important contributor. The extent to which such analogies may be valid is not certain: there is virtually no product RC_6H_4COOH corresponding to the cyclo-

hexylbenzoic acids.[3] Rate constant ratios were chosen to discriminate against ester formation, but this point deserves further study.

Induced decomposition leads experimentally to an over-all reaction effectively higher than first order, for first-order plots show curvature. A Nozaki and Bartlett plot[11] using our calculated runs at 0.01 and 0.3 M gave a line with slight curvature which might not be noticeable with actual data. The k_i/k_i ratio is 1.36. The raw data presented by Nozaki and Bartlett are very useful; recalculation of k_i/k_i by the same averaging method gave 0.61. It is also possible to obtain the ratio directly from initial rates: rate $= k_iP + k_iP^{3/2}$. By this method k_i/k_i is 1.3 for the experimental data,[11] or more than twice that estimated from the plot. From the calculated runs $k_i/k_i = 2.0$ for the first 800 sec (3% reaction) and 1.5 for the first 4000 sec (20% reaction). Hence the ratios observed are predicted to be sensitive to the fraction of reaction which is studied. That the data dissect poorly is a reflection of the fact that the assumed simple functional relationship is incorrect.

The problem with induced decomposition is to identify the reaction steps properly. Studies of other systems show a surprisingly varied pattern. In diethyl ether the major product is an ester, α-ethoxyethyl benzoate.[32] In cyclohexane the major product is p-cyclohexylbenzoic acid.[35] On the other hand, the 3-cyclohexenyl radicals from cyclohexene appears to give little induced reaction.[11,28,29] The oxidation steps in Table I, reactions 10 and 17, are still other proposed modes of induced reaction.[33] Products corresponding to p-cyclohexylbenzoic acid are formed in no more than trace amounts in the decomposition of benzoyl peroxide in benzene.

The problem may then be summarized as follows. What sort of induced reaction steps will on the one hand allow as small yields of benzoic acid as are actually observed and on the other hand be consistent in behavior with the reported results for substituted cyclohexyl and cyclohexenyl radicals? If reaction classes 23 and 25 are assigned larger rate constants, then the yield of benzoic acid is too high. If reaction classes 22, 24, and 26 are assigned larger rate constants, then the molecular weight of the residues is too low. One possible *ad hoc* solution would be to allow a small amount of polymerization and to increase the ester formation rates (to increase the amount of induced decomposition). However, a definitive answer must await further work with carefully chosen systems.

The major fate of the benzoyloxy radical is decarboxylation, and of the phenyl radical is addition to benzene. The CO_2 yield also represents the phenyl radical yield, and at all concentrations 85% or more of the phenyl radicals adds to benzene. In 0.3 M solution about two-thirds of the radical–radical termination reactions are combination and disproportionation of phenylcyclohexadienyl radicals; another 30% involve one phenylcyclohexadienyl radical plus some other radical. The proportion is even higher in dilute solution. In these respects the reaction is simple. However, the numerous other reactions occurring in small amounts contribute in sum a very important over-all influence on products.

The reason why biphenyl is not formed by combination of phenyl radicals (the predicted yield from this

route is 0.05 mole % in 0.3 M peroxide) is that addition to benzene effectively removes phenyl radicals so that the concentration is about 5×10^{-10} M, too low to permit coupling even at a diffusion-controlled rate. The concentration of phenylcyclohexadienyl radicals is 5×10^{-7}, of benzoyloxy radicals, 1×10^{-9}.
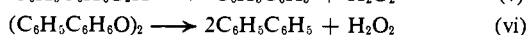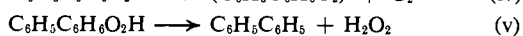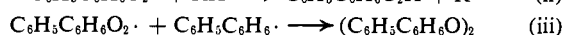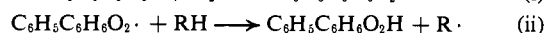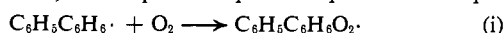
We have tested the mechanism of Table I on the system reported briefly by Eberhardt and Eliel in which dihydrobiphenyl was introduced initially.[41] Results are reported in Table VII. Comparison with Table V shows that the dihydrobiphenyl does relatively little in 0.01 M peroxide and that it just blends in to give a variety of products in 0.3 M peroxide. The reported biphenyl yields are rather higher, about 54% in roughly 0.2 M peroxide with 0.13 M dihydrobiphenyl. This suggests that the rate constants need further adjusting, but further decision must await additional quantitative data. The total dihydrobiphenyl reacts further by both hydrogen abstraction by benzoyloxy radicals (10%), by phenyl radicals (5%), and by alkyl radicals (43%), and it is also lost by benzoyloxy radical addition (42%). These figures are for 0.3 M peroxide with 0.2 M initially added dihydrobiphenyl at 90% completion.

Table VII. Product Yields with Initially Added Dihydrobiphenyl[a]

	Initial peroxide concn, M		
	0.010	0.30	0.30
	Initial dihydrobiphenyl concn, M		
	0.006	0.10	0.20
CO_2	179	113	97
Benzoic acid	11	44	48
Biphenyl	32	33	34
Dihydrobiphenyl	86	9	14
Phenyl benzoate	3	2	2
Tetrahydroquaterphenyl	52	4	5
Quaterphenyl	0	1	1
Terphenyl	0	0.5	0
Benzene (peroxide derived)	12	21	25
Esters C_{19}–C_{60} (phenyl)	10	51	61
(benzoyloxy)	6	41	53
Hydroxcarbons C_{30}–C_{60}	8	24	24

[a] Yields are reported at 90% reaction.

It is now possible to consider briefly the factors that determine isomer distribution in the arylation reaction. First the effect of oxidizing agents must be considered. It has been known for some time that biaryl yields are higher in nitrobenzene than in other solvents, and Eberhardt and Eliel[41] found that the reaction can be run in the presence of oxygen to give increased yields of biaryl. The mechanism of the oxygen effect has not been established, but eq i–vi represent plausible steps.

$$C_6H_5C_6H_6\cdot\ +\ O_2\ \longrightarrow\ C_6H_5C_6H_6O_2\cdot \qquad (i)$$

$$C_6H_5C_6H_6O_2\cdot\ +\ RH\ \longrightarrow\ C_6H_5C_6H_6O_2H\ +\ R\cdot \qquad (ii)$$

$$C_6H_5C_6H_6O_2\cdot\ +\ C_6H_5C_6H_6\cdot\ \longrightarrow\ (C_6H_5C_6H_6O)_2 \qquad (iii)$$

$$2C_6H_5C_6H_6O_2\cdot\ \longrightarrow\ (C_6H_5C_6H_6O_2)\ +\ O_2 \qquad (iv)$$

$$C_6H_5C_6H_6O_2H\ \longrightarrow\ C_6H_5C_6H_5\ +\ H_2O_2 \qquad (v)$$

$$(C_6H_5C_6H_6O)_2\ \longrightarrow\ 2C_6H_5C_6H_5\ +\ H_2O_2 \qquad (vi)$$

The hydrogen peroxide and perhaps the hydroperoxide and peroxide may go on to water plus further oxidation products. Equations ii and iii would be favored at low oxygen concentrations. The nitro group of nitrobenzene may also be involved in removing hydrogen atoms from arylcyclohexadienyl radicals.[42]

(41) M. Eberhardt and E. L. Eliel, *J. Org. Chem.*, 27, 2289 (1962).

The lack of reactivity of phenyl radicals with oxygen has been attributed to reversibility of eq vii but may alternatively be due simply to the fast reaction of phenyl radicals with the solvent as suggested.[41]

$$C_6H_5\cdot\ +\ O_2\ \longrightarrow\ C_6H_5OO\cdot \qquad (vii)$$

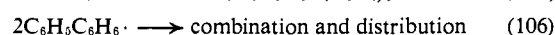We have then to consider the extent to which a substituent X may influence the rate at which $C_6H_5C_6H_5X\cdot$
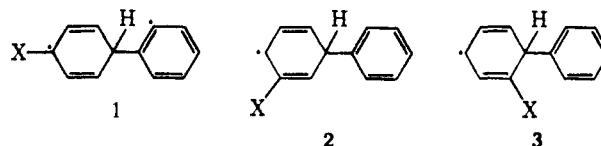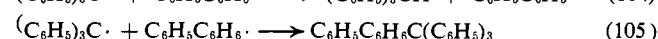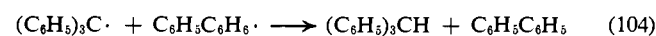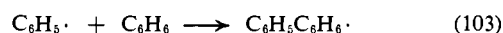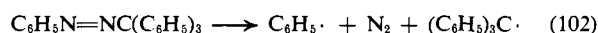

goes on to biphenyl rather than to other products. Unless the rates of all competing processes are closely similar, the biaryl product distribution must reflect imperfectly the relative rates of formation of **1**, **2**, and **3**.

The fact that **1** (X = H) gives p,p'-, and o,o'-tetrahydroquaterphenyl in a ratio of 55:43:2 suggests that steric factors may be important. If so, coupling of **1** might be somewhat slower than coupling of **3**. A comparison of relative isomer distributions in the presence and in the absence of oxygen gave identical isomer distributions for four different substituents X,[43] and this demonstrates an encouraging lack of discrimination in the competing reactions. The effect of steric factors on oxygen addition (eq i) is presumably small and the effects on relative rates of hydrogen atom removal from **1–3** are unknown, though probably not large.

One mildly disturbing feature remains. The yield of biaryl ranged up to 1.6 mole/mole of peroxide in one case, but was only 0.7 with nitrobenzene. It would be useful to know what other products are formed in order to provide a better check on the hypotheses.

A summary of the situation is as follows. (1) In reactions giving an almost stoichiometric yield of biaryl plus benzoic acid, it is probable that the radicals **1–3** have been oxidized almost quantitatively so that the biaryl distribution may be accepted as a measure of the relative arylation rates. (2) As the yield of biaryl becomes smaller, the opportunity for complications becomes greater. Until the major stoichiometry of a given reaction has been worked out, it cannot be known whether the biaryl isomer distribution reflects the relative arylation rates.

The thermal decomposition of phenylazotriphenylmethyl is a closely related problem. Hey and Perkins have identified the major products and suggest the mechanism in reactions 102–105.[44] In limiting cases the kinetics for this system are relatively simple to solve: let T stand for trityl, D for phenylcyclohexadienyl,

$$C_6H_5N{=}NC(C_6H_5)_3\ \longrightarrow\ C_6H_5\cdot\ +\ N_2\ +\ (C_6H_5)_3C\cdot \qquad (102)$$

$$C_6H_5\cdot\ +\ C_6H_6\ \longrightarrow\ C_6H_5C_6H_6\cdot \qquad (103)$$

$$(C_6H_5)_3C\cdot\ +\ C_6H_5C_6H_6\cdot\ \longrightarrow\ (C_6H_5)_3CH\ +\ C_6H_5C_6H_5 \qquad (104)$$

$$(C_6H_5)_3C\cdot\ +\ C_6H_5C_6H_6\cdot\ \longrightarrow\ C_6H_5C_6H_6C(C_6H_5)_3 \qquad (105)$$

$$2C_6H_5C_6H_6\cdot\ \longrightarrow\ \text{combination and distribution} \qquad (106)$$

$$2(C_6H_5)_3C\cdot\ \rightleftharpoons\ (C_6H_5)_3CC(C_6H_5)_3 \qquad (107)$$

(42) D. H. Hey, M. J. Perkins, and G. H. Williams, *Chem. Ind.* (London), 83 (1963).

(43) R. T. Morrison, J. Cazes, N. Samkoff, and C. A. Howe, *J. Am. Chem. Soc.*, 84, 4152 (1962).

(44) D. H. Hey and M. J. Perkins, *Tetrahedron Letters*, 445 (1963).

k_D for the total rate constant for all reactions between two phenylcyclohexadienyl radicals, k_T for the rate of eq 107 (presumed not reversible in the first of the approximations discussed), and $k_{cross} = k_{104} + k_{105}$. It is further assumed that reaction 103 is fast enough that all phenyl radicals are converted to phenylcyclohexadienyl radicals. Steady-state eq 108 and 109 then follow. Hence $T/D = (k_D/k_T)^{1/2}$ and the rates (not rate constants) for the two simple terminations 106 and 107

$$dD/dt = \text{rate } 102 - k_{cross}TD - 2k_DD^2 = 0 \qquad (108)$$

$$dT/dt = \text{rate } 102 - k_{cross}TD - 2k_TT^2 = 0 \qquad (109)$$

must be equal.[45] The ratio of cross products (CP) from reactions 104 and 105 to the phenylcyclohexadiene products (DP) (reaction 106) is given by eq 110. A limiting value of k_{cross} may be estimated as follows with $k_D = 1.5 \times 10^7$ (Table III) and $k_T = 3.6 \times 10^4$ [46] and

$$CP/DP = k_{cross}TD\ k_DD^2 = k_{cross}\ (k_Dk_T)^{1/2} \qquad (110)$$

setting CP/DP = 100 (on the assumption that if more than 1% of DP were formed they would be detectable), then $k_{cross} = 100(1.5 \times 3.6 \times 10^{11})^{1/2} = 7 \times 10^7$.

(45) The factor of 2 enters since two like radicals are removed, but the factor for product formation is 1 since only 1 mole of triphenylmethane, etc. is formed.

(46) Taken from the rates and activation energies in ref 4, p 530.

The same results were found by REMECH calculations using $k_{103} = 2000$ (Table I). If, however, reaction 107 is assumed rapidly reversible, then even with $k_{cross} = 1.5 \times 10^6$ there is less than 0.5% of DP formed. The reason for this pattern is that with (107) not reversible and with $k_{cross} = 0.5 \times 10^6$ there is a 25% yield of hexaphenylethane, but with (107) reversible, the yield of hexaphenylethane is small. A value of 10^6-10^7 for k_{cross} is certainly not exceptional, and the observed product distribution is thus readily predicted by reactions 102–107. Providing that the products of reaction 105 can be cracked quantitatively to biaryl and triphenylmethane, thermal decomposition of arylazotriphenylmethyls appears to be a most promising way for study of the arylation reactions.

Experimental Section

REMECH uses an iterative process.[13] Time intervals of 400 sec were used and radical concentrations were adjusted to 0.2%. The process was checked using intervals of 100 sec and adjustment to 0.02%. The yields of several minor products (<0.1%) showed appreciable differences, but major products all agreed to better than 1% relative. Run time was about 5 min per 300 equations set for about 35% of reaction on the IBM 709, and about 20 sec on the CDC 6400.
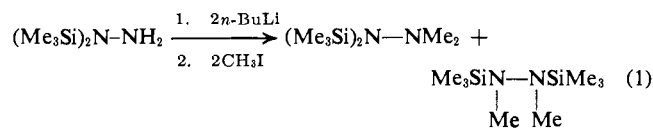
New Anionic Rearrangements. III. Catalytic Rearrangement of Organosilylhydrazines[1,2]

Robert West, Mitsuo Ishikawa, and Robert E. Bailey

Contribution from the Department of Chemistry, The University of Wisconsin, Madison, Wisconsin. Received February 10, 1967

Abstract: When organosilylhydrazines are treated with n-butyllithium or other strong bases, a rapid rearrangement of organosilyl groups from one nitrogen to another takes place. The rearrangement was studied by proton nmr spectroscopy. It occurs either with equimolar or catalytic amounts of base, proceeds to equilibrium, and is intramolecular. Bis(organosilyl)hydrazines and bis(organosilyl)methylhydrazines give approximately equal amounts of 1,1- and 1,2-bis(organosilyl) compounds at equilibrium. With organosilylphenylhydrazines, the isomer bearing a hydrogen on the nitrogen atom attached to the aromatic ring is favored at equilibrium. Several new organosilyl hydrazines were prepared in connection with these studies; their physical properties are reported.
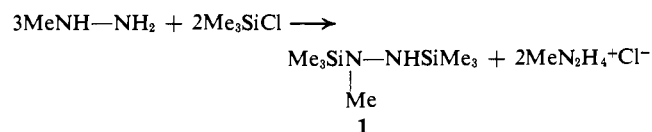
The anionic rearrangement of organosilyl hydrazines was first discovered for 1,1-bis(trimethylsilyl)-hydrazine.[2,3] This compound, upon treatment with 2 equiv of n-butyllithium followed by 2 equiv of methyl iodide, was transformed into a 1:1 mixture of the isomeric bis(trimethylsilyl)dimethylhydrazines.

$$(Me_3Si)_2N-NH_2 \xrightarrow[\text{2. } 2CH_3I]{\text{1. } 2n\text{-BuLi}} (Me_3Si)_2N-NMe_2 +$$

$$Me_3SiN-NSiMe_3 \qquad (1)$$
$$\begin{array}{cc} | & | \\ Me & Me \end{array}$$

In studying this reaction we were handicapped by the fact that the synthesis of bis(trimethylsilyl)hydrazine gives a mixture of isomers which is difficult to separate. Moreover, at the time there was no unequivocal way to establish which of the isomers had the 1,1 structure and which the 1,2.[4] We therefore turned to 1,2-bis-(trimethylsilyl)methylhydrazine (1) as a more convenient substrate.

1 can easily be prepared by reaction of methylhydrazine with trimethylchlorosilane, according to the directions given by Wannagat and Liehr.[5]

$$3MeNH-NH_2 + 2Me_3SiCl \longrightarrow$$

$$Me_3SiN-NHSiMe_3 + 2MeN_2H_4{}^+Cl^-$$
$$\begin{array}{c} | \\ Me \\ \mathbf{1} \end{array}$$

(2) Previous paper in this series: R. West, M. Ishikawa, and R. E. Bailey, *J. Am. Chem. Soc.*, **88**, 4648 (1966).
(3) R. E. Bailey and R. West, *ibid.*, **86**, 5369 (1964).

(4) For a discussion of the controversy concerning the structures of these isomers and its resolution see ref 2.
(5) U. Wannagat and W. Liehr, *Z. Anorg. Allgem. Chem.*, **299**, 341 (1959).