

TABLE VIII
 RETENTION RATIOS

Compound	G.I.c. method	Retention ratio	Compound	G.I.c. method	Retention ratio
Carbon tetrachloride	1	0.52	Chlorobenzene	1	3.78
	2	.66		2	4.00
	3	.67		3	3.67
	4	.43		4	3.52
	5	.71		5	4.32
Cyclohexane	1	.28	Chlorocyclohexane	1	3.04
	2	.50		<i>sec</i> -Butylbenzene	1
	4	.21			
Benzene	All	(1)			
Toluene	1	1.84			
	2	1.92			
	3	1.82			
	4	1.66			
	5	2.16			

column at 100° with a helium flow rate of 104 ml./min. Method 4 employed two 1-m. ODPN columns in series at 78° with a helium flow rate of 70 ml./min. Method 5 employed a 2-m. di-*n*-propyl tetrachlorophthalate column at 100° with a helium flow rate of 100 ml./min. Method 6 employed a 2-m. diisodecyl phthalate column A at 100° with a helium flow rate of 100 ml./min. Method 7 employed a 4.2-m. column packed with "Silicone Rubber on Chromosorb Regular, 30/60 mesh" obtained from Wilkens Instrument and Research, Inc., at 76° with a helium flow rate of 80 ml./min.

Correction factors were determined from gas chromatograms of standard solutions and conformed to the equation

$$\text{moles A/area A} = (\text{moles B/area B}) (\text{correction factor})$$

Correction factors were checked periodically and found not to be strongly influenced by the solvent mixture or slight changes in

temperature. In three cases "tailing" of the solvent was severe enough to necessitate special calibration. Such calibrations were obtained by adding the internal standard and benzene or chlorobenzene to the weighed solution which was used for the reaction.

Retention times relative to benzene are given for products and internal standards in Table VIII. Retention times for benzene under conditions 1, 2, 3, 4, and 5 were between 4.6 and 7.9 min. For further details of the analytical procedures see ref. 36.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

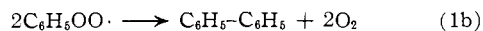
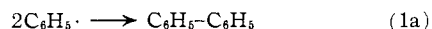
The Reactivity of Phenyl Radicals toward Molecular Oxygen¹

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Evidence is presented that phenyl radicals react less readily with molecular oxygen than do ordinary alkyl or benzylic-type radicals. It is argued that this reflects a pronounced polar effect in the reaction of radicals with oxygen, the transition state being pictured as $R^+ \cdots O-O$.

The coupling of phenyl radicals to give biphenyl is a process recognized to occur in the presence of oxygen, biphenyl being an important product in the vapor phase oxidation of benzene.^{3,4} However, the possibility exists



that the formation of biphenyl occurs *via* the intermediacy of phenylperoxy radicals. Numerous other examples suggest a low reactivity of oxygen toward

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(2) (a) Alfred P. Sloan Foundation Fellow, 1959-1963; (b) National Science Foundation Predoctoral Fellow, 1960-1962.

(3) J. Drillat, *Compt. rend.*, **252**, 1155 (1961); R. H. Kriebel and W. I. Denton, U. S. Patents, 2,415,101 (1947); 2,439,812 (1948).

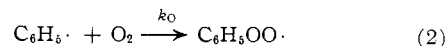
(4) This result is in sharp contrast with vapor phase studies involving alkyl radicals. In a typical experiment (W. C. Sleppy and J. G. Calvert, *J. Am. Chem. Soc.*, **81**, 769 (1959)) the presence of 1 cm. of oxygen reduced the yield of ethane by 96% in a flash photolysis of 5 cm. of azomethane at 25°

in the presence of 26 cm. of neopentane. If the value of k_1 for $2CH_3\cdot \xrightarrow{k_1} C_2H_6$ is taken as 3.6×10^{-11} cc./molecule-sec. at 25° (A. Shepp, *J. Chem. Phys.*,

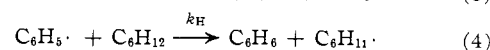
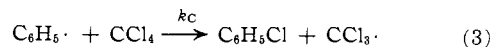
24, 939 (1956)), the termolecular reaction, $CH_3\cdot + O_2 + M \xrightarrow{k_0} CH_3O_2\cdot + M$, has a value of k_0 of 1×10^{-21} (cc./molecule)² sec.⁻¹ at 25° where M is neopentane. At 100 mm. pressure of M, the pseudo-second-order value of k_0 is 3.4×10^{-14} cc./molecule-sec. Under these conditions a methyl radical is 100 times as reactive as an oxygen molecule toward another methyl radical. For the dimerization reaction to become important (1% of methyl radicals reacting) the ratio of $[CH_3\cdot]/[O_2]$ would have to be greater than 0.5×10^4 or for 0.02 M oxygen the concentration of methyl radicals would have to exceed 1×10^{-6} M.

phenyl radicals. When the Meerwein reaction of styrene is conducted in the presence of oxygen the reaction products indicate that phenyl radicals add to styrene in preference to reacting with oxygen.⁵ Small amounts of oxygen actually increase the yields of the biaryls formed in homolytic arylation.⁶ The low efficiency of benzoyl peroxide in initiating autoxidation reactions of aralkyl hydrocarbons, but not in the initiation of polymerization processes, has been attributed to the low reactivity of the phenyl radical with molecular oxygen.⁷

We have measured the competition between reactions 1, 2, 3, and 4 by a study of the products of the



thermal decomposition of phenylazotriphenylmethane (PAT) at 60°, a process known to produce free phenyl radicals.⁸



(5) J. K. Kochi, *J. Am. Chem. Soc.*, **79**, 2942 (1957).

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TABLE I
PRODUCTS OF THE COMPLETE DECOMPOSITION OF PAT IN
CYCLOHEXANE (9.2 M) AND CARBON TETRACHLORIDE (10 M)
IN THE PRESENCE OF OXYGEN AT 60°

Solvent ^a	Total pressure, atm.	Oxygen pressure, atm.	Chlorobenzene ^b	Benzene ^b	k_O/k_C ^c	k_O/k_H ^c
CCl ₄	0.58	0	0.74	0.054
CCl ₄	1.00	0.4	.40	^d	1300	...
CCl ₄	2.1	1.5	.21	^d	1100	...
CCl ₄	3.1	2.5	.14	^d	1100	...
CCl ₄	4.1	3.5	.09	^d	1300	...
C ₆ H ₁₂	0.52	0	...	0.82
C ₆ H ₁₂	1.0	0.548	...	800
C ₆ H ₁₂	2.1	1.616	...	1400
C ₆ H ₁₂	3.1	2.612	...	1200
C ₆ H ₁₂	4.1	3.608	...	1400
C ₆ H ₁₂ -CCl ₄ ^e	1.0	~0.45	0.27	0.23	630 ^f	640 ^f

^a [PAT]₀ = 0.058 M in cyclohexane and 0.095 M in carbon tetrachloride. ^b Mole per mole of PAT. ^c See text. ^d Not measured. ^e Expt. performed by Mr. J. D. Hunt, [C₆H₁₂] = 4.54 M, [CCl₄] = 5.22 M, 0.1 M [PAT]₀. For a similar expt. in absence of O₂ see ref. 9. ^f Based on value of k_H/k_C of 0.98 calcd. from this expt.

In the absence or presence of oxygen in carbon tetrachloride or cyclohexane solution, reactions 2-4 compete so favorably with reaction 1 that no biphenyl can be detected in the decomposition of a solution originally 0.1 M in PAT. In the absence of oxygen, and in the presence of a mixture of cyclohexane and carbon tetrachloride, the ratio of chlorobenzene and benzene formed indicates that k_H/k_C is 1.08 ± 0.01 ,⁹ the total yield of benzene and chlorobenzene being about 0.75 mole per mole of PAT (0.1 M initial concentration). In pure carbon tetrachloride or in pure cyclohexane the yield of chlorobenzene or of benzene is decreased by the presence of oxygen, the effect of becoming more important at higher oxygen concentrations. Table I summarizes pertinent results.

The relative reactivities, k_O/k_C and k_O/k_H of Table I, were calculated by assuming that the yields of chlorobenzene were accurate measures of the extent of occurrence of reactions 3 and 4 and that the decrease in the yield of chlorobenzene or benzene in the presence of oxygen was due only to the occurrence of reaction 2. The ratios, k_O/k_H and k_O/k_C were calculated from the expressions

$$\frac{k_O}{k_C} = \frac{[\text{CCl}_4][0.74 - \text{C}_6\text{H}_5\text{Cl}]}{[\text{O}_2][\text{C}_6\text{H}_5\text{Cl}]}, \quad \frac{k_O}{k_H} = \frac{[\text{C}_6\text{H}_{12}][0.82 - \text{C}_6\text{H}_6]}{[\text{O}_2][\text{C}_6\text{H}_6]}$$

The concentration of oxygen in solution at a pressure of 1 atm. was taken as 0.016 M at 60°, the value reported for isooctane.¹⁰ Henry's law was used to calculate solubilities at other pressures. The applicability of Henry's law to carbon tetrachloride and hydrocarbons is well documented,¹¹ and the assumption that the solubility of oxygen is the same in most hydrocarbons is reported to be accurate to within about 20% relative error.¹²

As a cross-check on these assumptions it is gratifying that k_H/k_C calculated indirectly from the average value of $k_O/k_C = 1200$ and $k_O/k_H = 1200$ is 1.0 compared with the directly measured value of 1.1.⁹ The experiment in Table I, using mixed solvents, gave a value of 1.0 for k_H/k_C .

(9) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

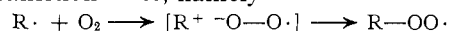
(10) C. B. Kretschmer, J. Nowakowska, and R. Wiebe, *Ind. Eng. Chem.*, **38**, 506 (1946).

(11) P. K. Frolich, E. J. Tauch, J. J. Hogan, and A. A. Peer, *ibid.*, **23**, 548 (1931); L. D. Derry, E. B. Evans, B. A. Faulkner, and E. C. G. Jelfs, *J. Inst. Petrol.*, **38**, 475 (1952).

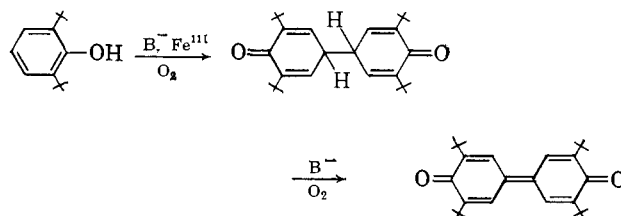
(12) M. Reznikovskiy, Z. Tarasova, and B. Dogadkin, *Zh. Obshchei Khim.*, **20**, 63 (1950).

Phenyl radicals react with oxygen about 10^8 times as readily as with cyclohexane at the same molar concentration. This relative reactivity sequence is quite different from that observed for simply alkyl, benzylic, or allylic radicals. The β -peroxystyryl radical derived from styrene reacts with a molecule of oxygen about 10^6 as readily as with another molecule of styrene at 60°.¹³ The competition between styrene and cyclohexane for the polystyrenyl radical at 60° is in the range of 2×10^4 with styrene being the most reactive.¹⁴ Thus toward a benzylic-type radical k_O/k_H is in the range of 10^{10} .

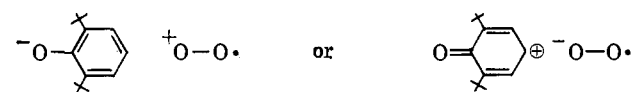
The difference between k_O/k_H for phenyl radicals (10^8) and benzyl-type radicals (10^{10}) may be a reflection of a much lower absolute value of k_O as well as a higher value of k_H for phenyl radicals. When the present results are considered in relation to the low efficiency noted for phenyl radicals in oxidation initiation and the formation of biphenyl in the presence of oxygen, it seems fairly certain that the difference in k_O/k_H values of roughly 10^7 must result at least partially, if not mainly, from a lower absolute value of k_O for phenyl radicals than for common types of alkyl radicals. It is felt that this reflects a significant polar contribution to the transition state, namely



The low value of k_O when R is phenyl is thus a reflection of the high energy content of phenyl carbonium ions. The same explanation presumably can be applied to the dimerization of 2,6-disubstituted phenols under conditions conducive to free radical intermediates.¹⁵



Again, the phenoxy radical is probably quite unreactive toward oxygen, in part because of its own resonance stabilization, but also in part because of the high energy contents of transition states involving electron transfer.¹⁶



Experimental

Reagents and General Procedure.—The PAT and other reagents have already been described as well as the general procedure for decomposition of PAT and analysis of the decomposition products for benzene and chlorobenzene.⁹

Decompositions in the Presence of Oxygen.—The PAT and solvent were placed in a pressure bottle in a Parr pressure reaction apparatus. After pressurization with oxygen the mixture was shaken mechanically and heated rapidly to 60°. Five minutes was required to bring the solution to this temperature. The temperature was controlled to $\pm 2^\circ$ by use of a calibrated thermocouple. After reaching 60° the pressure was maintained at ± 0.5 p.s.i. by admitting additional oxygen when needed. The decompositions were conducted for 4 hr., more than 10 half-lives of PAT at 60°. Benzene and chlorobenzene were measured by g.l.c. procedure 1.⁹ Analysis for biphenyl was conducted by use of a 1-m. silicone grease g.l.c. column at 157° in a Perkin-Elmer Model 154-D vapor fractometer. The presence of biphenyl in the decomposition products would have been readily detected if the concentration of biphenyl had been in the range of 0.001 M (2% based on PAT). No evidence of biphenyl was detected in any experiment.

(13) A. A. Miller and F. R. Mayo, *J. Am. Chem. Soc.*, **78**, 1017 (1956).

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

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(16) G. A. Russell, *Tetrahedron*, **5**, 101 (1959).