Directive Effects in the Attack of Phenyl Radicals on Carbon–Hydrogen Bonds[1,2]

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The reactivities of a wide variety of aliphatic carbon–hydrogen bonds toward the phenyl radical have been determined. In addition to alkanes and functionally substituted alkanes, the reactivities of allylic and benzylic-type hydrogen atoms have been studied. The reactivities of hydrogen atoms attached to atoms other than carbon have also been measured. Under the reaction conditions phenyl radicals reacted with aralkyl hydrocarbons to give almost exclusive benzylic attack. For terminal olefins an appreciable fraction of the phenyl radicals was consumed by addition processes. The present results represent the most extensive reactivity series available for a hydrogen abstraction process. The phenyl radical appears to be fairly free of polar effects in its reactions with saturated carbon–hydrogen bonds. Therefore the reactivity scale observed with a phenyl radical should be an important standard in assessing the importance of polar effects in other free radical processes.

Although aromatic substitution reactions involving phenyl radicals have been extensively investigated, the attack of phenyl radicals on saturated carbon–hydrogen bonds has received little attention. We have studied the reactions of phenyl radicals with a wide variety of carbon–hydrogen bonds by measuring the benzene and chlorobenzene formed as products of the competing reactions.

$$C_6H_5\cdot + RH \xrightarrow{k_H} C_6H_6 + R\cdot \qquad (1)$$

$$C_6H_5\cdot + CCl_4 \xrightarrow{k_C} C_6H_5Cl + \cdot CCl_3 \qquad (2)$$
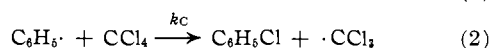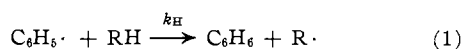
Phenyl radicals were generated by the thermal decomposition of phenylazotriphenylmethane (PAT) at 60°.[4] Relative reactivities were calculated from the expression

$$\frac{k_H}{k_C} = \frac{[C_6H_6][CCl_4]}{[C_6H_5Cl][RH]}$$

This approach can be justified only if (a) the kinetics of reactions 1 and 2 are first order in RH and CCl_4 and are of the same kinetic order in $C_6H_5\cdot$, (b) reactions 1 and 2 are the only sources of benzene and chlorobenzene, (c) the ratio $[CCl_4]/[RH]$ remains constant.

An experimental test of the first two assumptions is afforded by varying the concentrations of carbon tetrachloride and hydrogen-containing substrates.

Examination of Table I shows that varying $[CCl_4]/[RH]$ has no effect upon k_H/k_C. A further test of assumptions (a) and (b) can be made by considering the effect of initial PAT concentration on the observed value of k_H/k_C since an increase in the initial PAT concentration will increase the average phenyl radical concentration. If reactions 1 and 2 are not of the same kinetic order in phenyl radical concentration, or if either benzene or chlorobenzene is a product of some reaction that is second or higher order in radical concentration, e.g.

$$C_6H_5\cdot + (C_6H_5)_3CCCl_3 \longrightarrow C_6H_5Cl + (C_6H_5)_3CCCl_2\cdot \qquad (3)$$
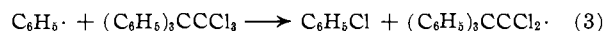
then the observed ratio k_H/k_C will vary in a systematic manner with a change in $[PAT]_0$. Examination of Table I shows that assumptions (a) and (b) again appear to be valid when subjected to this test.

By choice of the reaction conditions it was possible experimentally to hold the ratio $[CCl_4]/[RH]$ constant to within 1%. Decomposition of a dilute (0.1 M) solution of PAT in a mixture of carbon tetrachloride and a hydrocarbon of about equal reactivity will decrease the concentration of each solvent by no more than 1% if only one molecule of solvent is consumed per phenyl

TABLE I
DECOMPOSITION OF PHENYLAZOTRIPHENYLMETHANE (PAT) IN CARBON TETRACHLORIDE–HYDROCARBON SOLUTIONS AT 60°

Hydrocarbon (RH)	$[PAT]_0{}^a$	$\dfrac{[CCl_4]}{[RH]}$	$C_6H_6{}^b$	$C_6H_5Cl{}^b$	$\dfrac{k_H{}^c}{k_C}$
Toluene	0.096	0.552	0.22	0.33	0.28
Toluene	.096	.735	.20	.40	.27
Toluene	.096	.965	.18	.47	.27
Toluene	.096	1.26	.16	.51	.27
Cyclohexane	.096	0.748	.47	.29	1.08
Cyclohexane	.096	.985	.43	.34	1.10
Cyclohexane	.096	1.68	.33	.44	1.07
Cyclohexane	.051	0.985	.44	.36	1.07
Cyclohexane	.180	.985	.39	.30	1.02
Cyclohexane[d]	.096	.985	.38	.31	1.05
Cyclohexane[e]	.096	.985	.38	.32	1.02
Cyclohexane[f]	.047	f	.85	—	—
Carbon tetrachloride[f]	.048	f	.048	.83	—
Carbon tetrachloride[f]	.096	f	.054	.74	—
Carbon tetrachloride[f]	.144	f	.072	.68	—
Carbon tetrachloride[f]	.192	f	.080	.62	—
Biphenyl	.096	2.98	.061	.62	—
Triphenylamine	.096	8.00	.056	.63	—
Diphenyl ether	.096	1.01	.060	.49	—
Triphenylphosphine	.096	4.02	< .01	.04	—
Pyrrole	.096	2.15	.04	.50	—
Chlorobenzene[f]	.096	f	.07	—	—

[a] Mole liter⁻¹. [b] Mole per mole of PAT. [c] $k_H/k_C = [CCl_4][C_6H_6 - 0.05]/[RH][C_6H_5Cl]$. [d] Containing 1.2 M nitrobenzene. [e] Containing 1.5 M pyridine. [f] Single solvent.

radical generated; the concentration ratio of the two solvents will be changed even less. This will not necessarily be the case if chain reactions, such as reaction 4, occur.[5]

$$CCl_4 + RH \longrightarrow RCl + HCCl_3 \qquad (4)$$
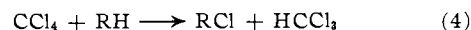
The yields of alkyl chlorides given in Table II for competitive experiments with carbon tetrachloride and aliphatic solvents show that this chain reaction is essentially eliminated by the relatively high concentration of trityl radicals present in the system.[4]

The choice of phenylazotriphenylmethane as the precursor to phenyl radicals was made deliberately and it is felt that the success of the present technique is largely due to this choice. Because of the stability of the triphenylmethyl radical it was expected that its

(1) Directive Effects in Aliphatic Substitution. XXIII.

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(4) It has been recently emphasized (G. A. Russell and R. F. Bridger, *Tetrahedron Letters*, 737 (1963); J. F. Garst and R. S. Cole, *ibid.*, 679 (1963)) that the thermolysis of PAT produces mainly free phenyl radicals.

(5) (a) G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959). (b) A discussion of the effects of such reactions on competitive experiments has been given by D. F. DeTar and D. V. Wells, *J. Am. Chem. Soc.*, **82**, 5839 (1960).

TABLE II

SELECTIVITY OF THE PHENYL RADICAL IN HYDROGEN ABSTRACTION REACTIONS AT 60°[a]

Substrate	$\frac{[CCl_4]}{[RH]}$	C_6H_6[b]	C_6H_5Cl[b]	Alkyl chloride (no.)[b]	$\frac{k_H}{k_C}$[c]	Av. k_H/k_C	Calcd.[d] k_H/k_C	$\frac{k_{\alpha-H}}{k_C} \times 10^2$	$\frac{k_\Delta}{k_C}$[e]
Alkanes									
Dimethylpropane	0.856	0.13[f]	0.47[f]	g	0.15	0.14	0.14	1.17 (1°)	
	.880	.12	.47		.13				
Tetramethylbutane	1.516	.14[f]	.59[f]	g	.23	.21	.21		
	0.895	.17	.52		.21				
	.858	.15	.46		.19				
Pentane	1.05	.30[f]	.42[f]	g	.62	.60	.60	0.98 (1°)	
	1.05	.28	.42		.58				
Hexane	0.904	.37[f]	.36[f]	0.16 (1)	.80	.80	.79	9.1 (2°)	
	.904	.36	.35		.80				
Heptane	1.01	.39[f]	.35[f]	.13 (2)	.98	.96	.97		
	1.01	.38	.35		.95				
Octane	1.12	.43[f]	.36[h]	.16 (3)	1.18	1.15	1.17		
	1.12	.41	.36		1.12				
Hexadecane	2.74	.39[f]	.37[f]	g	2.5	2.5	2.6		
	2.74	.39	.37		2.5				
2,2-Dimethylbutane	0.917	.20[i]	.45[i]	.03 (1)	0.31	0.31	0.30		
	.917	.20	.44		.31				
3-Methylpentane	.898	.36[i]	.31[i]	.16 (2)	.90	.90	.88	43 (3°)	
	.898	.35	.30		.90				
2-Methylpentane	.920	.38[i]	.34[i]	.18 (2)	.89	.86	.88		
	.920	.38	.36		.84				
3-Methylhexane	1.01	.40[i]	.33[i]	.23 (2)	1.07	1.07	1.06		
	1.01	.41	.34		1.07				
2,3-Dimethylbutane	0.900	.45[i]	.31[i]	.27 (1)	1.16	1.19	0.98		
	.900	.43	.28		1.22				
2,4-Dimethylpentane	1.03	.30[f]	.38[f]	.09 (1)	0.68	0.67	1.16		
	1.03	.30	.39		.66				
2,5-Dimethylhexane	1.03	.41[f]	.29[f]	.23 (2)	1.28	1.27	1.34		
	1.03	.42	.30		1.27				
2,2,3-Trimethylbutane	1.00	.29[j]	.34[h]	.15 (1)	0.71	0.71	0.59		
	1.00	.32[h]	.38[h,k]		.71				
2,2,4-Trimethylpentane	1.14	.19[f]	.44[l]	.03 (1)	.36	.34	.78		
	1.14	.19[i]	.48[h]		.33				
2,2,5-Trimethylhexane	1.25	.31[f]	.38[f]	.14 (1)	.85	.81	.96		
	1.25	.30[f]	.40[k]		.78				
2,3,4-Trimethylpentane	1.10	.37[f]	.35[h]	.07 (1)	1.01	.97	1.44		
	1.10	.37	.38		0.93				
Cycloalkanes									
Cyclopentane	0.651	0.50[f]	0.28[f]	0.1 (1)	1.04	1.04		10.4	
	.651	.50	.28		1.04				
Cyclohexane	(see Table I)			.2–0.3 (1)		1.08		9.0	
Cycloheptane	1.01	0.59[i]	0.24[i]	.17 (1)	2.3	2.3		16.4	
	1.01	.58	.23		2.3				
Cyclooctane	0.926	.59[j]	.17[f]	g	2.9	2.9		18.1	
	.926	.61[f]	.18[f]		2.9				
Methylcyclopentane	1.02	.45[f]	.26[f]	.07 (1)	1.57	1.56		70 (3°)	
	1.02	.46	.27		1.55				
Methylcyclohexane	1.16	.47[f]	.31[f]	.37 (3)	1.57	1.55		62 (3°)	
	1.16	.46	.31		1.53				
Alkenes									
cis-2-Butene	0.813	0.27[f]	0.20[f]	g	0.89	0.88	0.87	14.7 (1°)	1.14
	.945	.27	.24		.87				1.13
trans-2-Butene	.909	.21[f]	.23[f]	g	.63	.63	.87	10.5 (1°)	1.22
	.912	.21	.23		.63				1.23
2-Methyl-2-butene	1.09	.29[f]	.21[f]	g	1.24	1.24	1.30	13.8 (1°)	1.30
	1.09	.29	.21		1.24				1.30
2,3-Dimethyl-2-butene	1.85	.42[f]	.29[f]	g	2.4	2.3	1.74	19.2 (1°)	0.3
	1.85	.41	.30		2.2				.3
1-Butene	0.888	.17[f]	.16[f]	g	0.67	0.66	0.63	32 (2°)	2.3
	.885	.17	.16		.66				2.3
1-Pentene	1.15	.16[f]	.18[f]	g	.70	.73	.81	26 (2°)	2.6
	1.15	.17	.18		.77				2.6
2-Pentene	1.12	.34[f]	.26[f]	g	1.25	1.29	1.07		0.6
	1.12	.36	.26		1.33				.6
1-Octene	1.90	.21[f]	.22[f]	g	1.38	1.38	1.35	31 (2°)	2.8

Table II (*Continued*)

Substrate	$\dfrac{[\text{CCl}_4]}{[\text{RH}]}$	$C_6H_6{}^b$	$C_6H_5Cl{}^b$	Alkyl chloride (no.)^b	$\dfrac{k_H{}^c}{k_C}$	Av. k_H/k_C	Calcd.^{d} k_H/k_C	$\dfrac{k_{\alpha-H}}{k_C} \times 10^2$	$\dfrac{k_A{}^e}{k_C}$
	1.90	0.21	0.22		1.38				2.8
2-Octene	1.89	.27^f	.26^f	*g*	1.60	1.60	1.62		1.60
	1.89	.27	.26		1.60				1.60
2-Methyl-1-butene	1.14	.14^f	.11^f	*g*	0.93	0.93	1.06		5.2
	1.14	.14	.11		.93				5.2
3-Methyl-1-butene	0.89	.27^f	.13^f	*g*	1.50	1.47	1.26	141 (3°)	2.4
	.89	.26	.13		1.44				2.5
4-Methyl-2-pentene	1.97	.32^f	.38^f	*g*	1.40	1.45	1.69	96 (3°)	0.3
	1.97	.34	.38		1.50				.2
Propene	0.89	.07^f	.21^f	*g*					2.0
	.90	.07	.22						1.9
2,3,3-Trimethyl-1-butene	.97	.05^f	.10^f	*g*					5.9
	.97	.05	.10						5.9
3,3-Dimethyl-1-butene	1.08	.05^f	.21^f	*g*					2.5
	1.08	.05	.22						2.4
1,3-Pentadiene	1.04	.03^f	.03^f	*g*					24
	1.04	.03	.03						24
2-Phenylpropene	1.08	.01^f	.05^f	*g*					15
	1.08	.02	.05						15
1-Phenylpropene	1.35	.07^f	.14^f	*g*					5.2
	1.35	.06	.12						6.4
Cyclopentene	3.68	.37^f	.32^f	*g*	3.7	3.7		87	0.7
	3.68	.35	.31		3.6				1.1
	3.67	.36	.31		3.7				0.9
	3.67	.36	.31		3.7				.9
	0^m	.58							
Cyclohexene	4.20	.42^f	.35^f	*g*	4.4	4.4		101	.0
	4.20	.41	.34		4.4				.0
	4.07	.40	.33		4.3				.2
	4.07	.42	.34		4.4				.0
	0^m	.72							
3-Phenylpropene	1.37	.27^i	.17^i	*g*	1.77	1.82		91	2.5
	1.37	.27	.16		1.88				2.7
2,5-Dimethyl-2,4-hexadiene	2.50	.30^f	.22^f	*g*	2.8	2.9		24	2.6
	2.50	.30	.20		3.1				3.1

Alkynes

Substrate	$\dfrac{[\text{CCl}_4]}{[\text{RH}]}$	$C_6H_6{}^b$	$C_6H_5Cl{}^b$	Alkyl chloride (no.)^b	$\dfrac{k_H{}^c}{k_C}$	Av. k_H/k_C	Calcd.^{d} k_H/k_C	$\dfrac{k_{\alpha-H}}{k_C} \times 10^2$	$\dfrac{k_A{}^e}{k_C}$
Propyne	0.660	0.15^f	0.23^f	*g*	0.3	0.3		10	1.1
1-Butyne	.888	.30^f	.21^f	*g*	1.06	1.02		50	1.0
	.830	.30	.21		0.99				0.9
2-Butyne	.928	.36^f	.34^f	*g*	.85	0.87		14.5	.14
	.873	.39	.33		.90				.08

Aralkyl hydrocarbons and derivatives

Substrate	$\dfrac{[\text{CCl}_4]}{[\text{RH}]}$	$C_6H_6{}^b$	$C_6H_5Cl{}^b$	Alkyl chloride (no.)^b	$\dfrac{k_H{}^c}{k_C}$	Av. k_H/k_C	Calcd.^{d} k_H/k_C	$\dfrac{k_{\alpha-H}}{k_C} \times 10^2$	$\dfrac{k_A{}^e}{k_C}$
t-Butylbenzene	1.43	0.10^f	0.60^k	*g*	0.12	0.11		1.2 ($^k\beta$)	
	0.814	.11	.49		.10				
Toluene	(see Table I)					.27		9.0	
p-Chlorotoluene	1.07	.18^f	.48^f	*g*	.29	.29		9.7	
	1.07	.18	.46		.30				
m-Chlorotoluene	1.07	.15^f	.44^f	*g*	.24	.24		8.0	
	1.07	.16	.48		.25				
p-Phenoxytoluene	0.972	.15^f	.36^f	*g*	.27	.26		8.7	
	.972	.15	.37		.26				
p-Nitrotoluene	1.07	.14^f	.44^f	*g*	.22	.22		7.3	
	1.07	.14^i	.44^f		.22				
p-Xylene	1.03	.34^n	.37^n	*g*	.81	.79		13.2	
	1.03	.33	.37		.78				
Mesitylene	0.959	.30^f	.28^f	*g*	.85	.85		9.4	
	.959	.29	.27		.85				
Ethylbenzene	1.27	.32^n	.42^n	*g*	.82	.84		41	
	1.27	.34	.43		.86				
Cumene	1.16	.37^n	.39°	*g*	.95	.93		87	
	1.16	.36	.39		.92				
Diphenylmethane	1.21	.40^f	.31^f	*g*	1.37	1.4		69	
	1.21	.40	.31		1.37				
	1.75	.35	.38		1.38				
	4.45	.25	.57		1.56				
Triphenylmethane	2.51	.42^f	.26^f	0.1^p	3.6	3.5		350	
	3.76	.36	.33		3.5				

TABLE II (*Continued*)

Substrate	$\dfrac{[CCl_4]}{[RH]}$	$C_6H_6{}^b$	$C_6H_5Cl{}^b$	Alkyl chloride (no.)^b	$\dfrac{k_H{}^c}{k_C}$	Av. k_H/k_C	$\dfrac{k_{\alpha-H}}{k_C} \times 10^2$
Indan	1.92	0.52^i	0.29^i	0	3.1	3.1	72
	1.92	.50	.27		3.2		
Tetralin	2.13	.55^i	.23^i	0	4.6	4.8	111
	2.13	.60	.23		5.1		
Hexamethylbenzene	6.67	.30^f	.55^f	0	3.0	3.1	17
	6.65	.30	.50		3.3		

Alkyl substituted heteroaromatics							
3-Picoline	1.01	0.12^i	0.51^i	0	0.14	0.12	4.0
	1.01	.10	.52		.10		
4-Picoline	1.01	.11^i	.53^i	0	.11	.12	4.0
	1.01	.12	.53		.13		
s-Collidine	1.10	.21^i	.47^i	0	.37	.37	4.1
	1.10	.21	.47		.37		
2,5-Dimethylpyrazine	0.575	.18^f	.22^f	0	.34	.33	5.5
	1.13	.15	.35		.32		
2-Methylfuran	0.926	.12^f	.26^f	0	.25	.25	8.3
	.926	.12	.26		.25		
3-Methylthiophene	.985	.14^f	.37^f	0	.24	.24	8.0
	.985	.14	.37		.24		
2-Methylthiophene	.987	.24^f	.42^f	0	.45	.44	15
	.987	.23	.41		.43		
Di-2-thienylmethane	1.87	.52^f	.21^f	0	4.2	4.2	210
	1.86	.53	.21		4.3		
N-Methylpyrrole	2.30	.08^f	.36^f	0	0.3	0.3	10
2,5-Dimethylpyrrole	1.05	.43^f	.29^f	0	1.38	1.43	24
	1.05	.46	.29		1.48		

Substituted alkanes							
Chloroform	1.00	0.67^f	0.18^f	0	3.4	3.2	320
	0.496	.74	.11		3.1		
	0^m	.87	< .01		..		
Methylene chloride	0.990	.31^f	.52^f	0	0.49	0.48	24
	.505	.43	.41		.47		
	0^m	.77	< .01		..		
Methyl chloride	0.839	.11^f	.61^f	0	.08	.07	2.3
	.866	.10	.64		.07		
	0^m	.21	< .01		..		
Trimethylamine	0.888	.65^f	.16^f	0	3.3	3.2	36
	1.73	.53	.26		3.2		
N,N-Dimethylaniline	0.536	.61^f	.11^f	0	2.7	2.8	47
	1.07	.54	.17		3.1		
	2.18	.23	.25		1.6		
	5.00	.38	.42		3.9		
Thioanisole	1.79	.16^f	.51^f	0	0.39	0.39	13
	2.46	.14	.56		.40		
Methanol	0.105	.44^l	.32^l	0	.13	.13	4.3
	.140	.41	.36		.14		
Dimethyl ether	.888	.21^f	.51^f	0	.28	.28	4.7
	.888	.21	.51		.28		
Anisole	.510	.13^f	.44^f	0	.093	.094	3.1
	1.02	.10	.54		.095		
Acetone	0.096	.43^l	.21^l	0	.17	.17	2.8
	.152	.40	.29		.18		
Diethyl ketone	1.09	.43^f	.32^f	0	1.29	1.30	31
	0.880	.47	.28		1.32		
Diisopropyl ketone	2.95	.29^f	.48^f	0	1.5	1.3	59
	2.95	.24	.47		1.2		
Acetic acid	0.297	.20^f	.51^f	0	0.087	0.086	2.9
	.297	.20	.52		.086		
Methyl acetate	.491	.15^l	.56^l	0	.088	.086	2.9
	.334	.18	.51		.085		
Methyl benzoate	.259	.07^f	.26^f	0	.02	.01	0.3
	.259	.06	.25		.01		
Dimethyl malonate	.475	.23^f	.47^f	0	.18	.18	9.0 (2°)
	.475	.23	.46		.19		
2,4-Pentanedione	2.13	.18^f	.57^f	0	.49	.48	15 (2°)
	1.78	.20	.57		.47		
Isobutyronitrile	0.555	.47^f	.32^f	0	.73	.73	67

TABLE II (*Continued*)

Substrate	$\dfrac{[CCl_4]}{[RH]}$	C_6H_6[b]	C_6H_5Cl[b]	Alkyl chloride (no.)[b]	$\dfrac{k_H}{k_C}$[c]	Av. k_H/k_C	$\dfrac{k_{\alpha-H}}{k_C} \times 10^2$
	0.555	0.46	0.31		0.73		
Propionitrile	.312	.43f	.31f	g	.38	0.37	17.0
	.312	.41	.31		.36		
Acetonitrile	.109	.34f	.35f	g	.090	.090	3.0
	.109	.35	.36		.091		
Tetramethylsilane	.706	.22f	.40f	g	.30	.29	2.4
	.706	.21	.40		.28		
Phenyltrimethylsilane	1.08	.14f	.46f	g	.21	.21	2.3
	1.08	.14	.46		.21		
2-Nitropropane	0.560	.26f	.47f	g	.25	.25	19.1
	.560	.27	.50		.25		
Nitroethane	.299	.33f	.45f	g	.19	.19	8.0
	.299	.34	.45		.19		
Nitromethane	.115	.23f	.44f	g	.047	.047	1.6
	.115	.23	.44		.047		
Dimethyl sulfoxide	.092	.23f	.40f	g	.041	.039	0.65
	.148	.17	.47		.038		
			Hydrogen bonded to heteroatoms				
Diphenylsilane	1.53	0.65f	0.12f	0.7p	7.7	7.7	390
	1.53	.61	.11		7.8		
Triphenylsilane	6.99	.36f	.46f	.09p	4.7	4.8	480
	10.00	.30	.51		4.9		
Diphenylamine	7.10	.21f	.51f	g	2.2	2.3	230
	10.0	.19	.57		2.5		
Diphenylphosphine	7.16	.40f	.03f	p,q	80	60	6000
	10.4	.26	.05		40		
			Deuterium substituted compounds				
Acetone-d_6	0.096	0.17l	0.27l	g	0.043	0.041	0.68
	.128	.15	.32		.040		
Toluene-α-d_3	1.00	.09f	.50f	g	.07r	.06r	2
	0.372	.11	.32		.06r		

a 0.096 mole l.⁻¹ of PAT. b Mole per mole of PAT. c Per molecule; $k_H/k_C = [CCl_4][C_6H_5 − 0.05]/[RH][C_6H_5Cl]$. d See text. e $k_A/k_C = [CCl_4][0.75 − C_6H_6 − C_6H_5Cl]/[RH][C_6H_5Cl]$. f By g.l.c., method 1. g None detected. h By g.l.c., method 3. i By g.l.c., method 2. j Determined by ultraviolet absorption. k By g.l.c., method 6. l By g.l.c., method 5. m Single solvent. n By g.l.c., method 4. o By g.l.c., method 7. p Chloroform. q Maintaining 6 mmoles of diphenylphosphine in 4 ml. of carbon tetrachloride *without* PAT at 60° for 11 hr. gave *ca.* 6 mmoles of chloroform. r Corrected for isotopic purity of 95%.

concentration would reach a reasonable steady-state value in the solutions and that it would prevent the occurrence of chain processes such as the chlorination re-
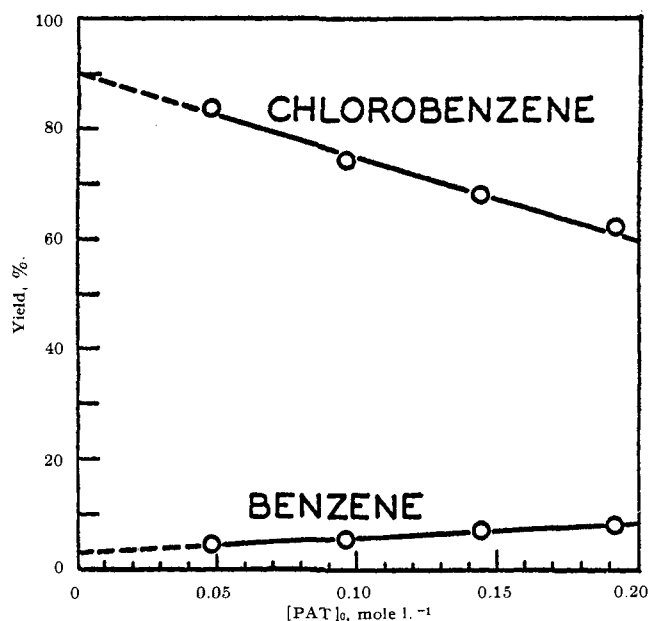
Fig. 1.—Decomposition of PAT in carbon tetrachloride at 60°; effect of initial PAT concentration of yields of benzene and chlorobenzene.

actions referred to previously and the polymerization of olefins. The presence of the triphenylmethyl radical must greatly reduce the probability of benzene or chlorobenzene being formed by reactions of the phenyl radical with some other transient species. Thus, during most of the reactions, the triphenylmethyl radical should have efficiently trapped R· and CCl_3· formed in reactions 1 and 2. Of course, some phenyl radicals were also trapped by the triphenylmethyl radical before they could enter into these reactions. In the presence of aromatic reactants the triphenylmethyl radical must destroy products of the addition of phenyl radicals to aromatic rings before they can react with more phenyl radicals to yield benzene.[4]

As shown in Table I, the relative reactivities of toluene and carbon tetrachloride did not change when the toluene–carbon tetrachloride ratio was varied, and the competition between cyclohexane and carbon tetrachloride was unaffected by the addition of nitrobenzene or pyridine to the solution. No strong solvent effects, such as those observed with the chlorine atom,[6] have as yet been detected in the reactions of the phenyl radical. Further examples of the constancy of k_H/k_C with changing [CCl₄]/[RH] may be found in Table II.

The decomposition of highly purified PAT in carbon tetrachloride solution at 60° produces small amounts of benzene. Figure 1 shows the benzene and chlorobenzene yields as functions of [PAT]₀. Extrapolation to an infinite dilution of PAT results in yields of 3% ben-

(6) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987, 4997, 5002 (1958).

$$
\begin{array}{ccc}
\underset{H}{\overset{CH_3}{\underset{|}{\overset{|}{CH_3C}}}}\!\!-\!\!-\!\!\underset{CH_3}{\overset{H}{\underset{|}{\overset{|}{CCH_3}}}}
&
\underset{CH_3}{\overset{CH_3}{\diagup}}C\underset{H\ \ H}{\overset{CH_2\ \ CH_3}{\diagdown\diagup}}C\underset{CH_3}{\overset{CH_3}{\diagdown}}
&
\underset{CH_3}{\overset{H}{\diagup}}C\underset{CH_3\ \ CH_2}{\overset{CH_2\ \ CH_3}{\diagdown\diagup}}C\underset{H}{\overset{CH_3}{\diagdown}}
\end{array}
$$

Expt. k_H/k_C	1.19	0.67	1.27
$\dfrac{\text{Expt. } k_H/k_C}{\text{Calcd. } k_H/k_C}$	1.21	0.58	0.95

zene and 90% chlorobenzene. We believe these data are evidence for cage processes in the decomposition of PAT which consume phenyl radicals and form benzene. Possible reactions might be

$$C_6H_5N\!=\!NC(C_6H_5)_3 \longrightarrow (C_6H_5)_4C + N_2 \qquad (5)$$
$$C_6H_5N\!=\!NC(C_6H_5)_3 \longrightarrow C_6H_6 + \text{9-phenylfluorene} + N_2 \quad (6)$$
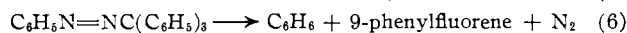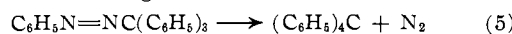
Besides benzene formed in a cage reaction, additional benzene (2.4%) is formed in the decomposition of 0.1 M PAT in pure carbon tetrachloride, presumably by the attack of phenyl radicals on PAT or upon its initially formed decomposition products. We have therefore corrected all data for this cage process by subtracting 5% from the observed yield of benzene ($[PAT]_0 = 0.1\ M$).

$$\frac{k_H}{k_C} = \frac{[CCl_4][C_6H_6 - 0.05]}{[RH][C_6H_5Cl]}$$

The application of this correction to solvent mixtures cannot be completely justified, but it is pertinent that the reactivity of pure carbon tetrachloride toward phenyl radicals is of the same order of magnitude as the total reactivity of the carbon tetrachloride–hydrocarbon mixtures investigated. Additional support for the assumption that the benzene correction is independent of the substrate–solvent system is derived from the results of the decomposition of PAT in carbon tetrachloride solutions of diphenyl ether, triphenylamine, biphenyl, and pyrrole, and in pure chlorobenzene. The yield of benzene is between 4 and 7% in all cases (see Table I).

Relative reactivities are summarized in Table II. Although not a primary object of this study, the data of Table II also provide a crude measure of the reactivity of olefins toward the addition of phenyl radicals. For the decomposition of 0.096 M PAT in saturated solvents the total yields of benzene and chlorobenzene varied between 70 and 80%. When PAT is decomposed in olefinic solvents this yield is decreased, presumably due to reaction 7.
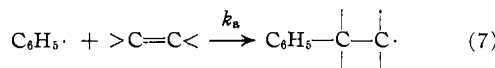
$$C_6H_5\cdot + >C\!=\!C< \xrightarrow{\ k_a\ } C_6H_5\!-\!\overset{|}{\underset{|}{C}}\!-\!\overset{|}{\underset{|}{C}}\cdot \qquad (7)$$

Table II also summarizes the ratio k_A/k_C for each olefin as calculated by the equation

$$\frac{k_A}{k_C} = \frac{[CCl_4](0.75 - [C_6H_5] - [C_6H_5Cl])}{[RH][C_6H_5Cl]}$$

Discussion

Reactivities of Alkanes.—Calculated reactivities as given in Table II (column 8) are based on the assumptions that the reactivities of single carbon–hydrogen bonds relative to the carbon tetrachloride molecule are: primary hydrogen atoms of methyl groups attached to quaternary carbon atom, 0.0117; all other primary hydrogen atoms, 0.0098; secondary hydrogen atoms, 0.091; tertiary hydrogen atoms, 0.43. These values give an average $1°:2°:3°$ reactivity series of 1–1.2: 9.3:44. These reactivities were determined by solving simultaneous equations for the normal alkanes, alkanes with a single branch, neopentane, and hexamethylethane.
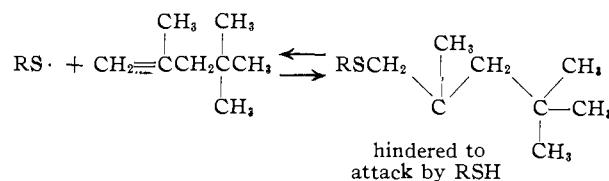
The reactivity series $(1°:2°:3°)$ is in the same range as that observed for t-butoxy radicals at $40°$ $(1°:2°:3° = 1:8\text{–}12:44)^7$ and methyl radicals at $182°$ in the vapor

phase $(1°:2°:3° = 1:7:50)$.[8] The phenyl radical is considerably more selective than the chlorine atom at $25°$ $(1°:2°:3° = 1:3.6:4.2)$,[6] although the exothermicities of both abstraction reactions are approximately the same.

The calculated total reactivities agree fairly well with the experimental reactivities of more complicated alkanes except for those compounds wherein two $3°$-carbon atoms or a $3°$- and a $4°$-carbon atom are situated in a 1,3-arrangement. For these compounds (2,4-dimethylpentane, 2,2,4-trimethylpentane, 2,3,4-trimethylpentane) the experimental reactivities are substantially less than the calculated reactivities. Comparing 2,3-dimethylbutane, 2,4-dimethylpentane, and 2,4-dimethylhexane, we find that the lower and higher homologs have "normal" reactivities which are considerably higher than 2,4-dimethylpentane. Even if the methylene group of 2,4-dimethylpentane is ignored, a total reactivity of 0.98 is predicted for the molecule. It is concluded that the preferred conformation of the molecule, which forces the $3°$-hydrogen atoms into close proximity, interferes with the approach of the phenyl radical to $3°$-position. A similar conclusion is reached upon examination of the homologous series triptane, isooctane, and 2,2,5-trimethylhexane.

The anomalously low reactivities of 2,4-dimethylpentane and isooctane toward the t-butoxy radical have been noted previously by Brook and interpreted in a similar manner.[9] Evidence for the low reactivity of the $3°$-carbon–hydrogen bond of isooctane has been presented by rate[10a] and product[10b] studies of other free radical processes.

The anomalous reactivity of α-diisobutylene[11] in free radical addition reactions with mercaptans suggests the occurrence of an analogous steric effect

$$
RS\cdot + CH_2\!=\!\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}CH_2\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}CH_3 \ \underset{\longrightarrow}{\overset{\longleftarrow}{\ }}\ RSCH_2\underset{\substack{\text{hindered to}\\\text{attack by RSH}}}{\overset{CH_3}{\diagup}}C\underset{CH_3}{\overset{CH_2}{\diagdown\diagup}}C\overset{CH_3}{\underset{CH_3}{-}}CH_3
$$

Reactivities of Cycloalkanes.—The reactivity sequence (per hydrogen atom) of cyclooctane > cycloheptane > cyclopentane > cyclohexane is consistent with the reactivity sequences known for chlorine atoms and methyl radicals[6,12] (see Table III).

Reactivities of Alkenes and Alkynes.—Calculated reactivities for 12 olefins are given in Table II. These calculated reactivities were obtained using average bond reactivities $(k_{\alpha-H}/k_C)$ of 0.145, 0.30, and 1.20 for $1°$, $2°$, and $3°$ allylic positions, respectively. Vinyl hydrogen atoms were considered to have no reactivity and all nonallylic positions were assumed to have the same reactivities as the corresponding types of hydrogen atoms in alkanes. Table II also lists the individual reactivities of the allylic hydrogen atoms as calculated from the above assumptions.

(7) C. Walling and W. Thaler, J. Am. Chem. Soc., **83**, 3877 (1961).

(8) A. F. Trotman-Dickenson, Quart. Rev. (London), **7**, 198 (1953).

(9) J. H. T. Brook, Trans. Faraday Soc., **53**, 327 (1957).

(10) (a) C. E. Frank and A. U. Blackham, Ind. Eng. Chem., **46**, 212 (1954); J. P. Wibaut and A. Strang, Koninkl. Ned. Akad. Wetenschap., Proc., **54B**, 229 (1951); (b) F. F. Rust and D. O. Collamer, J. Am. Chem. Soc., **76**, 1055 (1954); A. L. J. Beckwith, J. Chem. Soc., 2248 (1962).

(11) E. S. Huyser and J. D. Taliaferro, J. Org. Chem., **28**, 1676 (1963).

TABLE III

RELATIVE REACTIVITIES OF VARIOUS TYPES OF CARBON–HYDROGEN BONDS TOWARD COMMON RADICALS AND ATOMS IN SOLUTION

Type of bond	Phenyl,[a] 60°	Methyl, 65°	t-Butoxy,[b] 40°	Chlorine,[c] 40°	Bromine,[d] 40°
Primary aliphatic	0.11–0.13	—	0.1	0.8–0.9	—
Secondary aliphatic	1.01	—	0.8–1.2	~3	<0.009[e]
Tertiary aliphatic	4.8	—	4.4	3.6	0.3, 0.105[f]
Cyclopentane	1.15	—	1.38	2.1	—
Cyclohexane	1.00	—	1.50	2.0	0.004,[g] 0.003[f]
Cycloheptane	1.82	—	—	2.2	—
Cyclooctane	2.0	—	—	3.2	—
Primary allylic	1.61	0.60[h]	1.2–2.0	—	—
Secondary allylic	3.3	6.4[h]	6.1–9.3	—	35–40[f]
Tertiary allylic	13.3	26[h]	17.6	—	—[z]
Cyclopentene (α)	9.7	0.97[i]	38	—	600[j]
Cyclohexene (α)	11.2	.18[i]	37	—	160[j]
Toluene (α)	(1)	(1)[k]	(1)	(1)	(1)
Ethylbenzene (α)	4.6	4.1[k]	3.2	2.5[l]	17
Cumene (α)	9.7	12.9[k]	6.8	5.5[l]	37
Diphenylmethane (α)	7.7	—	4.7[m]	2.0[l]	10
Triphenylmethane (α)	39	—	9.6[m]	7.2[l]	18
Indan (α)	8.0	8.3[k]	—	4.4[l]	36[j]
Tetralin (α)	12.3	11.5[k]	—	4.1[l]	36[j]

[a] Present work. [b] Ref. 7. [c] Ref. 6. [d] Ref. 19. [e] 25°, G. A. Russell and H. C. Brown, J. Am. Chem. Soc., 77, 4025 (1955). [f] 80°, N-bromosuccinimide, carbon tetrachloride; C. Walling, A. Rieger, and D. D. Tanner, J. Am. Chem. Soc., 85, 3129 (1963). [g] 80°, ref. 29a. [h] R. P. Buckley and M. Szwarc, Proc. Roy. Soc. (London), A240, 396 (1957). Allylic reactivities were calculated relative to toluene from the relationship $k_{toluene}/k_{isooctane}$ = 2.5; see R. P. Buckley, F. Leavitt, and M. Szwarc, J. Am. Chem. Soc., 78, 5557 (1956). [i] Ref. 13. [j] Using N-bromosuccinimide, ref. 14. [k] Ref. 17. [l] Ref. 29b. [m] C. Walling and B. B. Jacknow, J. Am. Chem. Soc., 82, 6108 (1960).

A comparison of the reactivities of 2,3-dimethyl-2-butene (k_H/k_C = 2.3) and 2,5-dimethyl-2,4-hexadiene (k_H/k_C = 2.9) shows that activation of allylic carbon hydrogen bonds in the conjugated diene exceeds that of the alkene by only about 25%.

The high reactivities of hydrogen atoms α to triple bonds is consistent with previous observations involving the methyl radical.[8]

Assigning the nonallylic hydrogen atoms of cyclopentene (total reactivity 3.7) and cyclohexene (total reactivity 4.4) the values observed in cyclopentane (0.104 per hydrogen) and cyclohexane (0.090 per hydrogen) leads to reactivities per allylic hydrogen of 0.87 for cyclopentene and 1.01 for cyclohexene. Apparently, the allylic positions of both cyclopentene and cyclohexene are considerably more reactive than acyclic 2°-allylic hydrogen atoms. Szwarc and co-workers have pointed out that toward the methyl radical at 65° cyclohexene is less than one-fifth as reactive as cyclopentene in hydrogen abstraction,[13] an effect also observed in competitive bromination using N-bromosuccinimide.[14]

Table II also lists the approximate reactivities of a number of olefins to the addition of phenyl radicals. The results are in good qualitative agreement with data for the addition of methyl and trichloromethyl radicals,[15,16] including the very low reactivity observed for cyclohexene.

Reactivity of Aralkyl Hydrocarbons.—The decomposition of dilute solutions of PAT in aromatic solvents, such as chlorobenzene, or in mixtures of carbon tetrachloride with diphenyl ether, biphenyl, triphenylamine, or pyrrole, did not produce benzene substantially in excess of the 5.4% observed in pure carbon

tetrachloride. This is in agreement with the conclusion that the thermal decomposition of PAT in aromatic solvents gives rise only to aromatic arylation.

$$C_6H_5N\!\!=\!\!NC(C_6H_5)_3 + ArX \longrightarrow$$
$$C_6H_5\!-\!C_6H_5X + N_2 + (C_6H_5)_3CH \quad (8)$$
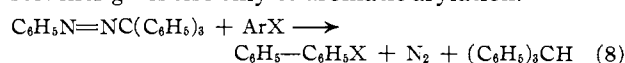
by a process involving the free phenyl radical.[4] The reactivities of aromatics toward the phenyl radical are not great enough that aromatic substitution can efficiently compete with abstraction reactions involving carbon tetrachloride or alkyl side chains. Thus (Table I) the total yield of benzene and chlorobenzene formed in the decomposition of 0.1 M PAT in a mixture of equal parts of toluene and carbon tetrachloride is 65% (vs. about 75% when toluene is replaced by an alkane) and 55% in a mixture containing toluene and carbon tetrachloride in a ratio of 1.8 to 1. Probably the low phenyl radical concentrations, resulting from the use of dilute solutions of PAT at 60°, are responsible for the low yields of aromatic phenylation products observed in this work.

The reactivities of benzylic hydrogen atoms are summarized in Tables II and III. The relative reactivities of the 1°, 2°, and 3° hydrogen atoms of toluene, ethylbenzene, and cumene of 1.0:4.6:9.7, respectively, indicate that the phenyl radical has a selectivity similar to that of the methyl radical (1:4:13) at 65°.[17] The phenyl radical is considerably more selective than chlorine atoms or t-butoxy radicals (Table III), but less selective than the peroxy radical at 90° (1.0:8:13),[18] the bromine atom at 40° (1:20:40:),[14,19] or the trichloromethyl radical at 40° (1:50:260).[19]

The occurrence of possible polar effects[20] in abstraction reactions of phenyl radicals was investigated by considering the reactivities of mesitylene, p-phenoxytoluene, p-chlorotoluene, m-chlorotoluene, and p-nitrotoluene. These compound displayed nearly equal

(12) A. S. Gordon and S. R. Smith, J. Phys. Chem., 66, 521 (1962).

(13) J. Gresser, A. Rajbenbach, and M. Szwarc, J. Am. Chem. Soc., 83, 3005 (1961).

(14) G. A. Russell and K. M. Desmond, ibid., 85, 3139 (1963).

(15) M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," Butterworths Sci. Publ., London, 1959, p. 271.

(16) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 254.

(17) J. A. Meyer, V. Stannet, and M. Szwarc, J. Am. Chem. Soc., 83, 25 (1961).

(18) G. A. Russell, ibid., 78, 1047 (1956).

(19) G. A. Russell and C. DeBoer, ibid., 85, 3136 (1963).

(20) G. A. Russell, J. Org. Chem., 23, 1407 (1958).

TABLE IV

REACTIVITIES OF HYDROGEN ATOMS α TO AROMATIC SYSTEMS

Aromatic system	2,2'-Diarylmethane	1-Methyl	2-Methyl	3-Methyl	4-Methyl	2,5-Dimethyl	2,4,6-Trimethyl
			Relative reactivities[a]				
Benzene	69	9.0	9.0	9.0	9.0	13.2	9.0
Pyridine	—	—	—	4.0	4.0	—	4.1
Pyrazine	—	—	—	—	—	5.5	—
Furan	—	—	8.3	—	—	—	—
Thiophene	210	—	14.7	8.0	—	—	—
Pyrrole	—	10	30[b]	12[b]	—	24	—
Indole			37[b]	220[b]			

[a] Per reactive hydrogen, $k_{\alpha-H}/k_C \times 100$. [b] Preliminary results of Mr. J. D. Hunt.

reactivities and yielded a Hammett $\rho\sigma$ plot with a ρ of only -0.1. Thus, the phenyl radical is rather insensitive to polar effects.

Reactivities of Heteroaromatics.—The reactivities of methyl-substituted heteroaromatics have not been previously investigated to any extent in free radical substitution reactions. Our present results indicate that the reactivities of these compounds can vary significantly and in a manner for which no explanation is immediately obvious. Table IV summarizes pertinent data in terms of single hydrogen reactivities.

Benzylic hydrogen atoms are more than twice as reactive toward phenyl radicals as the α-hydrogens of 3- or 4-picoline. The lower reactivities of the picolines had been recognized previously in reactions involving the t-butoxy radical.[21] However, in view of the absence of a significant polar effect in the reactions of phenyl radicals with substituted toluenes, it seems unlikely that this reactivity difference should be ascribed to a polar effect as has been suggested.[21] Hydrogen atoms α to the pyrazine nucleus, 2-substituted furan, and 3-substituted thiophene are all less reactive than benzylic hydrogen atoms. However, α-hydrogen atoms at the 2-positions of pyrrole and thiophene are 2–3 times as reactive as the corresponding benzylic hydrogen atoms. There is no correlation between the measured reactivities and the resonance energies of the parent heteroaromatics as measured by heats of hydrogenation. Moreover, delocalization energies as calculated by the Hückel molecular orbital method using commonly accepted parameters[22] for α and β did not in any manner approximate the observed reactivity series.[23]

Reactivities of Functionally Substituted Aliphatics.— The primary objective of this work was to establish a comprehensive reactivity scale of the reactivities of hydrogen atoms α to common functional groups toward the phenyl radical. Because of the absence of significant polar effects, this reactivity series toward the phenyl radical should reflect closely the bond dissociation energies of the carbon–hydrogen bonds being broken. In Table V the reactivities of compounds of the types ZCH_3, $ZRCH_2$, ZR_2CH, Z_2CH_2, and Z_3CH are summarized (Z = functional group, R = alkyl).

The relative reactivities of secondary and tertiary carbon–hydrogen bonds α to functional groups were calculated by assigning all β-hydrogens the reactivities of the paraffinic analogs.
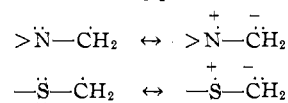
As shown in Table V, most substituents have small effects on the reactivities of α-hydrogen atoms toward phenyl radicals. Most substituents (nitro, methylsulfinyl, acetyl, cyano, carbomethoxy, carboxyl, chloro) have activating influence of less than fourfold whereas phenyl or vinyl substituents activate by about tenfold.

Of the substituents investigated only the amino (enhancement 31–40) and mercapto (enhancement 11–14) had large effects on reactivity. Both of these substituents presumably stabilize the incipient alkyl radical by resonance of the type

$$>\overset{\cdot}{N}-\overset{\cdot}{C}H_2 \leftrightarrow >\overset{+}{N}-\overset{-}{C}H_2$$

$$-\overset{\cdot}{\underset{\cdot\cdot}{S}}-\overset{\cdot}{C}H_2 \leftrightarrow -\overset{+}{\underset{\cdot\cdot}{S}}-\overset{-}{C}H_2$$

Examination of Table V reveals that decreased enhancement is provided by the functional group as alkyl substitution is increased at the α-carbon atom. Thus the rate enhancement due to Z in the series $Z-CH_3$, $Z-CH_2CH_3$, $Z-CH(CH_3)_2$, decreases in that order when Z is nitro, cyano, phenyl, or vinyl. The ketone series appears to deviate slightly in the case of diethyl ketone. Substitution of one, two, or three functional groups for hydrogen atoms in the series ZCH_3, Z_2CH_2, Z_3CH does not produce a consistent trend, the enhancement being about the same throughout the series when Z is phenyl, but increasing when Z is a chlorine atom. The meager enhancement observed for the methylene hydrogens of 2,4-pentanedione and dimethyl malonate serve as further examples of the low contribution of enolate resonance discussed below.

The reactivities observed with functionally substituted alkanes suggest that many substituents either do not appreciably stabilize a substituted methyl radical or that the transition state for hydrogen abstraction is insensitive to resonance stabilization of the final radical. When the reactivity sequence observed for the alkanes is considered, it appears that the transition state does appreciably reflect resonance stabilization of the incipient free radical and one might conclude that functional substituents, such as the carbonyl group, do not appreciably interact with a free electron at the α-position. However, we do not believe this apparently straightforward interpretation to be correct. If all the variation in reactivity of the unsubstituted alkanes toward the phenyl radical is assumed to occur in the energy of activation, it is found that the Evans–Polanyi equation[24]

$$\Delta E_a = \alpha \Delta(\Delta H_r)$$

is followed with $\alpha = 0.4$.[25] This indicates a fairly selective radical involving considerable bond breaking in the transition state for hydrogen abstraction.[26] Aralkyl hydrocarbons (toluene, ethylbenzene, p-xylene, cumene) also fit a similar plot with α again equal to about 0.4. However, all of the benzylic hydrogen atoms are about one-ten-thousandth as reactive as would have been predicted from the Evans–Polanyi relationship which holds for the alkanes. Thus, a

(21) K. M. Johnston and G. H. Williams, J. Chem. Soc., 1447 (1960).

(22) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(23) These calculations were performed by Mr. E. T. Strom.

(24) M. G. Evans and M. Polanyi, Trans. Faraday Soc., 34, 11 (1938).

(25) Using bond dissociation energies given by T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths Sci. Publ., London, 1958.

(26) G. A. Russell, J. Am. Chem. Soc., 79, 3871 (1957).

Table V
RELATIVE REACTIVITIES OF CARBON–HYDROGEN BONDS α TO FUNCTIONAL SUBSTITUENTS

Substituent (Z)	1°-Hydrogen ZCH₃	2°-Hydrogen Z(CH₃)CH₂	Z₂CH₂	3°-Hydrogen Z(CH₃)₂CH	Z₃CH
Alkyl	1^b	1^c	1^c	1^d	1^d
Phenyl	7.7	4.5	7.6	2.0	8.1
Vinyl	12.4^e	3.3^e	—	2.8^e	—
Chloro	2.0	—	2.6	—	7.4
Dimethylamino	31	—	—	—	—
Phenylmethylamino	40	—	—	—	—
Thiophenyl	11	—	—	—	—
Thiomethyl^k	14	—	—	—	—
Hydroxy	3.7	—	—	—	—
Methoxy	4.0	—	3.1^k	—	—
Methylperoxy^k	2.4	—	—	—	—
Phenoxy	2.7	—	—	—	—
Acyl	2.4^f	3.4^g	1.65^h	1.37^i	—
Carboxyl	2.5	—	—	—	—
Benzoyloxy	Very low	—	—	—	—
Carbomethoxy	2.5^j	—	0.99	—	—
Cyano	2.6	1.87	—	1.56	—
Trimethylsilyl	2.1	—	—	—	—
Phenyldimethylsilyl	2.0	—	—	—	—
Nitro	1.37	0.88	—	0.44	—
Methylsulfinyl	0.56	—	—	—	—

^{a} Relative reactivity of α-carbon–hydrogen bond divided by reactivity of same type bond in alkanes. ^{b} $k_{α-H}/k_C = 0.0117$. ^{c} $k_{α-H}/k_C = 0.091$. ^{d} $k_{α-H}/k_C = 0.43$. ^{e} Average values. ^{f} Acetone. ^{g} Diethyl ketone. ^{h} 2,4-Pentanedione. ^{i} Diisopropyl ketone. ^{j} Methyl acetate: reaction assumed to occur only at acyl group; see M. H. J. Wijnen, J. Chem. Phys., 27, 710 (1957). ^{k} Preliminary results of Mr. J. D. Hunt.

benzylic hydrogen atom with a bond dissociation energy of 78 kcal. mole⁻¹ is only one-fifth as reactive as a 3°-aliphatic carbon–hydrogen bond with a bond dissociation energy of about 90 kcal. mole⁻¹. If the differences in bond dissociation energies of 1°, 2°, and 3° carbon–hydrogen bonds in alkanes and in aralkyl hydrocarbons are completely due to delocalization of the free electron in the final radical, it is obvious that such delocalization must be much more highly developed in the transition state for the rupture of a carbon–hydrogen bond in an alkane than for a benzylic carbon–hydrogen bond, despite the fact that both series of hydrocarbons fit Evans–Polanyi expressions with α equal to about 0.4.

An alternative explanation is that variation of the bond dissociation energies of 1°, 2°, and 3° carbon–hydrogen bonds in alkanes reflects relief in steric strain due to the decrease in nonbonded interactions as the tetrahedral carbon atom approaches a planar configuration (B-strain).[27] This relief in steric strain would be most apparent at small carbon–hydrogen bond extensions while delocalization of an electron, as in the case of the benzyl radical, would not become important until the carbon–hydrogen bond is extensively ruptured. In other words, the Morse curve for 3°-aliphatic and 1°-benzylic carbon–hydrogen bonds have quite different shapes and would actually cross when plotted in a manner so that zero-point energies and ground-state bond lengths coincide.[28] The phenyl radical apparently gives rise to a transition state with sufficient bond breaking so that the relief in strain associated with the conversion of a tetrahedral to a planar tertiary carbon atom is quite well developed but without sufficient bond breaking for extensive electron delocalization, such as in an incipient benzyl or enolate radical to be highly developed. This interpretation of reactivities

readily explains the anomalous observation that toward the chlorine atoms (little bond breaking) cyclohexane and other 2°-aliphatic hydrogen atoms are more reactive than 1°-benzylic hydrogen atoms while toward the bromine atom (extensive bond rupture) the reverse reactivity sequence is observed.[29]

Although the amount of resonance stabilization of the incipient radicals is not large, we feel that the differences in reactivity of functionally substituted alkanes toward the phenyl radical do represent a measure of the ultimate amount of delocalization possible. The over-all trends indicated in Table III support this view. The present results offer a much wider scope of hydrogen transfer reactivities of functionally substituted alkanes than has been previously available. In addition, it appears reasonable to expect that the reactivity of numerous other substituted alkanes and perhaloalkanes toward the phenyl radical will be obtained. It is particularly interesting to compare the reactivities of α-carbon–hydrogen bonds in substituted alkanes

$$C_6H_5· + CH_3–X \xrightarrow{k_H} C_6H_6 + ·CH_2X \qquad (9)$$
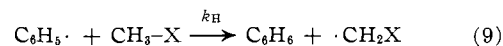
with the reactivities of substituted olefins in copolymerization.

$$R· + CH_2=CHX \xrightarrow{k_A} R—CH_2CHX \qquad (10)$$
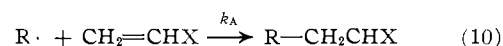
If both reactions measure the ability of X to stabilize a free radical on the adjacent carbon atom, a parallelism between the two measurements should exist. It has been postulated that Q-values, obtained by the Q–e scheme, reflect the intrinsic reactivity of olefins toward polymer radicals and hence the resonance stabilization of the substituted alkyl radical.[30] Table VI emphasizes that only a crude proportionality exists between these quantities.

Upon study of Table VI we have concluded that the Q-values of olefins reflect in part the resonance stabilization of the resulting radicals ($RCH_2ĊHX$, etc.) but

(27) H. C. Brown, Science, 103, 385 (1946); H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson, and K. L. Nelson, J. Am. Chem. Soc., 75, 1 (1953); L. S. Bartell, J. Chem. Phys., 32, 827 (1960).

(28) M. Szwarc in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p. 91.

(29) (a) G. A. Russell and H. C. Brown, J. Am. Chem. Soc., 77, 4578 (1955); (b) G. A. Russell, A. Ito, and D. G. Hendry, ibid., 85, 2976 (1963).

(30) T. Alfrey and C. C. Price, J. Polymer Sci., 2, 101 (1947).

TABLE VI

COMPARISON OF Q-VALUES[a] AND REACTIVITIES TOWARD THE PHENYL RADICAL

X	Q			$k_{\alpha-H}/k_C$, C$_6$H$_5$·		
	XCH=CH$_2$	X(CH$_3$)C=CH$_2$	X$_2$C=CH$_2$	XCH$_3$	X(CH$_3$)CH$_2$	X$_3$CH$_2$
Benzoyloxy	0.06	0.05[b]	..	0.03	..	..
Methylsulfinyl	.06	..	..	.07	..	..
n-Alkyl	.02[c]	0.03[d]	0.03[d]	.11[e]	1.0[e]	1.0[e]
t-Butyl	.01	..	..	.13	..	..
Chlorine	.04	0.04	0.22	.26	..	2.7
Trimethylsilyl	.03	..	..	.27	..	..
Acetyl	.69	1.5	..	.31	3.4[f]	1.7
Carboxyl	1.15	2.3	..	.32	..	..
Carbomethoxy	0.42	0.74	..	.32	..	1.0
Cyano	.60	1.1	20	.33	1.9	..
4-Pyridyl	.82	..	..	.44	..	..
Ethoxyl	.03	..	..	.52[g]	..	..
p-Nitrophenyl	1.6	..	..	.81	..	..
m-Chlorophenyl	1.0	..	..	.89	..	..
p-Anisyl	1.4	..	..	.97[h]	..	..
Phenyl	1.00[i]	0.98	1.6	1.00[i]	4.6	7.7
p-Chlorophenyl	1.0	..	..	1.1	..	..
9-Carbazyl	0.44	..	..	1.1[j]	..	..
Thiophenyl	.34	..	..	1.4	..	..
p-Tolyl	1.1	..	..	1.5	..	..
Vinyl	2.4	3.3	..	1.6[k]	3.3[k]	..
Isopropenyl	3.3	5.9	..	~1.6[k]	3.3[k]	..
Ethynyl	0.69	0.54	..	1.6	5.6	..
2-Thienyl	2.9	..	..	1.7	..	23.

[a] L. J. Young, J. Polymer Sci., 54, 411 (1961).　[b] Isopropenyl acetate.　[c] 1-Hexene.　[d] 2-Methylpropene.　[e] n-Pentane.　[f] Diethyl ketone.　[g] Methyl ether.　[h] p-Phenoxytoluene.　[i] Assumed.　[j] N-Methylpyrrole.　[k] Average values for alkenes.

that the Q–e treatment has not made a clean-cut separation of such effects from polar effects in polymerization reactions. Olefins with substituents capable of stabilizing carbanions (X = carbomethoxy, carboxyl, acetyl, cyano, p-nitrophenyl) have been assigned too high Q-values while olefins with substituents capable of stabilizing an α-carbonium ion (X = alkoxy, thiophenyl, thiophenyl, alkyl) have been assigned values too low.

Reactivities of Hydrogen Atoms Attached to Heteroatoms.—The reactions of phenyl radicals were investigated with a series of compounds of the type $(C_6H_5)_n$ MH$_{(3 \text{ or } 4) - n}$, where M = C, Si, N, and P. The results indicate that, other things being equal, the ease of scission of M–H bonds decreases in the order >P–H > ⩾Si–H ~ >N–H > ⩾C–H. Triphenylsilane is 1.4 times as reactive as triphenylmethane while diphenylsilane is 5.6 times as reactive as diphenylmethane. Diphenylamine is 1.6 times as reactive as diphenylmethane on a molecular basis or 3.3 times as reactive per hydrogen atom. Diphenylphosphine is approximately 30 times as reactive as diphenylamine. As Table II shows, the total yields of benzene and chlorobenzene in experiments with diphenylphosphine are very low, benzene being essentially the only product formed. The very low yield of chlorobenzene observed upon decomposition of PAT in a carbon tetrachloride solution of triphenylphosphine (Table I) suggests that addition of phenyl radicals to trivalent phosphorus is an efficient process. Mayo has proposed that this addition is extremely fast and reversible.[31] The reactions of diphenylphosphine and triphenylphosphine with PAT in carbon tetrachloride solution are also further complicated by the occurrence of ionic reactions between the phosphines and the solvent.[32]

Deuterium Isotope Effect.—The isotope effect (k_H/k_D) in the attack of phenyl radicals upon toluene-

(31) F. R. Mayo, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961, p. 41Q.

(32) C. Screttas and A. F. Isabell, J. Org. Chem., 27, 2563 (1962); F. Ramirez, N. B. Desai, and N. McKelvie, J. Am. Chem. Soc., 84, 1745 (1962); R. Rabinowitz and R. Marcus, ibid., 84, 1312 (1962).

α-d_3 and acetone-d_6 was found to be 4.5 ± 0.5 and 4.2 ± 0.4, respectively. It had been previously reported that k_H/k_D was in the range 3.1–5.5 for the abstraction reaction of phenyl radicals with toluene at 110–116°.[33] These values compare with isotope effects between ≳7 (125°) and 10 (60°) reported for the methyl radical.[33,34] The isotope effects observed for both methyl and phenyl radicals indicate a fairly selective radical involving extensive bond breaking in the transition state for hydrogen abstraction.[26] The values of α in the Evans-Polanyi equation for saturated alkanes are 0.4 and 0.5 for phenyl and methyl radicals,[8] respectively. The values of α for attack of both phenyl and methyl radicals are also consistent with a transition state involving considerable breaking of the carbon–hydrogen bonds.[29a]

A plot of log k_H/k_C observed for phenyl radicals at 60° in the liquid phase against log k for hydrogen abstraction by methyl radicals at 182° in the vapor phase[8] gives a general linear correlation with unity slope for 13 functionally substituted alkanes, 8 alkanes, 5 alkenes, and 2 alkynes wherein data are available for both abstraction processes. The phenyl radical thus appears to have in general a reactivity and selectivity similar to that of the methyl radical in reactions involving the abstraction of a hydrogen atom from a carbon–hydrogen bond. While absolute rate constants are not yet known, the results of a recent study of reactions of phenyl radicals with alkanes in the gas phase agree qualitatively with this conclusion.[35]

Experimental

Reagents.—Liquids were purified by fractional distillation when necessary. Fractionations at atmospheric pressure were conducted in a Todd distillation apparatus using a monel spiral column. A 16-in. spinning band column was used for distillations at reduced pressure. All compounds were examined for impurities by g.l.c.; solids were examined as carbon tetrachloride solutions to ascertain the absence of volatile impurities which

(33) S. H. Wilen and E. L. Eliel, ibid., 80, 3309 (1958).

(34) L. Herk and M. Szwarc, ibid., 82, 3558 (1960).

(35) F. J. Duncan and A. F. Trotman-Dickenson, J. Chem. Soc., 4672 (1962).

TABLE VII

EFFECT OF VARIOUS TREATMENTS ON THE DECOMPOSITION PRODUCTS OF PAT IN CARBON TETRACHLORIDE[a]

Sample no. and treatment	Yields before treatment			Yields after treatment		
	C_6H_6[b]	C_6H_5Cl[b]	C_6H_6/C_6H_5Cl	C_6H_6[b]	C_6H_5Cl[b]	C_6H_6/C_6H_5Cl
1[c]	0.054[d]	0.74	0.073	0.045	0.64	0.070
2[e]	.18[f]	.18[f]	1.00	.053	.72	.074
3[e]	.072	.73	0.099	.056	.74	.076
3[g]	.072	.73	.099	.045	.56	.080
3[h]	.072	.73	.099	.049	.67	.073
3[i]	.072	.73	.099	.052	.71	.073

[a] Decompositions were conducted for 4 hr. at 60°, 0.096 M PAT.   [b] Mole per mole of PAT; determined by g.l.c. method 1.
[c] Treated with activated manganese dioxide; expt. performed by Mr. J. D. Hunt.   [d] Benzene values by g.l.c. and ultraviolet absorption were identical.   [e] Treated with hydrogen chloride.   [f] This yield is based on total weight of impure PAT; sample was 45% PAT.
[g] Treated with silver nitrate.   [h] Treated with lead dioxide.   [i] Treated with hydrogen peroxide in acetic acid.

would interfere with the determination of products. Alkanes were examined by ultraviolet spectroscopy and g.l.c. for the presence of aromatics and were treated with sulfuric acid until transparent in the ultraviolet region. Carbon tetrachloride was Mallinckrodt reagent grade and was passed through silica gel before use; examination by g.l.c. showed less than 0.1% impurity. Most compounds contained less than 1% impurity. Due to the larger number of compounds used in this study, the Ph.D. thesis of R. F. Bridger should be consulted for the history of each reagent, as well as relative retention times for the g.l.c. analyses described below.[36]

Acetone-d_6.[37]—Acetone (60 g. of Baker analyzed reagent, dried) was equilibrated at room temperature for 36 hours with 50 g. deuterium oxide and 0.2 g. potassium carbonate. The product was then fractionally distilled through a 27 × 1.4 cm. column packed with 0.25 in. glass helices. This procedure was repeated four more times to yield acetone-d_6 in 79% yield. Isotopic purity was estimated to be 97%.[38]

Toluene-α-d_3 was prepared according to the procedure of Renaud and Leitch[39] and was shown by n.m.r.[40] to have an isotopic purity of 95.0 ± 0.1%.

Phenylazotriphenylmethane (PAT) was prepared by the method of Cohen and Wang.[41] Preparation of N-phenyl-N'-tritylhydrazine from triphenylchloromethane and phenylhydrazine proceeded smoothly, but oxidation of the hydrazine to PAT was occasionally found to be incomplete. The oxidation was conducted by allowing an excess of hydrogen peroxide in saturated aqueous sodium bicarbonate solution to react with an ethereal solution of the hydrazine. The degree of oxidation was followed by withdrawing a small portion of the ether layer and introducing anhydrous hydrogen chloride to the sample. The hydrazine hydrochloride was precipitated if oxidation was incomplete. The sample of PAT (no. 1 of Table VII) used for the determination of all reactivities was prepared in the following manner. N-Phenyl-N'-tritylhydrazine (180 g.) in 200 ml. of ether was stirred for 5 hr. at room temperature with 90 ml. (50% excess) of 30% hydrogen peroxide in 1000 ml. of saturated bicarbonate solution. The ether layer was washed with 5% sodium hydroxide, water, and dried. Treatment of a small sample of the ether solution with anhydrous hydrogen chloride produced a cloudiness. The solvent was evaporated at reduced pressure and the product was washed with cold ethanol and recrystallized from a methylene chloride–ethanol mixture to give 93 g. of impure PAT. This material was treated as before with 90 ml. of 30% hydrogen peroxide. After stirring for 4 hr., treatment of a sample of the ether solution produced no cloudiness, PAT, 60 g., m.p. 111–112° dec., was isolated as before and dried 24 hr. at 2 mm. pressure. Melting point was found to be a poor criterion of purity for PAT (see sample 2 below). For this reason the products of decomposition of 0.096 M PAT in carbon tetrachloride at 60° were used as a measure of purity (see Table VII). Storage for 8 months at 0–10° produced no change in the decomposition products of sample 1.

The formation of benzene upon decomposition of PAT in carbon tetrachloride could possibly arise from the presence of N-phenyl-N'-tritylhydrazine or some other impurity. For this reason, PAT samples of varying degrees of purity were prepared in order to determine the effect of various oxidizing agents on the ratio benzene/chlorobenzene produced in carbon tetrachloride at 60°.

Sample 2 was prepared by treating 21 g. of N-phenyl-N'-tritylhydrazine with 16 ml. of 30% hydrogen peroxide for 5 hr. Hydrogen chloride treatment of the ether solution showed that large quantities of the hydrazine still remained. The product, 14 g., m.p. 112–114°, was found to contain 55% of the hydrazine, determined as the hydrochloride. Sample 3 was prepared by adding 60 ml. of 30% hydrogen peroxide in two portions to 80 g. of N-phenyl-N'-tritylhydrazine during a 10-hr. period to give 28 g. of PAT, m.p. 110–112°. Portions of sample 3 were treated with silver nitrate (46 hr.),[42] lead dioxide (1 hr.),[43] and hydrogen peroxide in acetic acid (7 hr.).[44] Ether solutions (2 g. per 100 ml.) of samples 2 and 3 were treated with anhydrous hydrogen chloride for 10 min. and filtered. After treatment, the various samples were decomposed at 60° in carbon tetrachloride. A summary of the data in Table VII shows that none of these treatments significantly altered the benzene/chlorobenzene ratio.

Decomposition Procedure.—Solutions of the two substrates were made by weight in glass-stoppered flasks and thoroughly mixed; PAT was weighed into an ampoule of about 10-ml. capacity and a volume of the solvent solution necessary to make a 0.096 M PAT solution was added to the ampoule. Solid compounds were weighed directly into the ampoule and carbon tetrachloride was added volumetrically from a calibrated pipet. Gaseous substances were transferred to the ampoule, previously loaded with PAT and carbon tetrachloride, by means of a vacuum line equipped with a standard bulb of known volume. Reaction mixtures were degassed and sealed under vacuum while frozen. The sealed tubes were placed in an oil bath maintained at 60 ± 0.1° for 4 hr. (more than ten half-lives of PAT). After reaction, ampoules were stored in Dry Ice until analyses were performed. Immediately before g.l.c. analysis each ampoule was broken and a solution of an internal standard was added.

Analytical Procedures.—Ultraviolet absorption spectra were measured with a Beckman DK-2 spectrophotometer. Gas chromatograms were obtained with a Perkin–Elmer vapor fractometer Model 154-D, and areas were measured with a plainmeter.

Determination of benzene by ultraviolet absorption[45] was useful in those reaction mixtures containing only substances easily separable from carbon tetrachloride and benzene by distillation. Carbon tetrachloride was accurately measured into the sample in such quantity as required to give an absorbance of 0.5 to 1.0. Carbon tetrachloride and benzene were codistilled and the absorbance at 262 mμ of the distillate was measured. The number of moles of benzene was calculated from the molarity on the basis of the total volume of carbon tetrachloride. The results of this method were found to agree within ±1% relative error with those of g.l.c. methods.

All columns for g.l.c. were constructed of 0.25-in. metal tubing. Firebrick was treated with hexamethyldisilazane.[46] Method 1 for gas chromatographic determination of benzene and chlorobenzene employed a 1-m. 3,3'-oxydipropionitrile column (ODPN), 20% by weight on 80/100 mesh firebrick, in series with a 1-m. di-n-propyl tetrachlorophthalate column,[47] 10% on 80/100 mesh firebrick, at 86° with a helium flow rate of 80 ml./min. measured at ambient conditions. Method 2 employed the ODPN column described above with a 2-m. diisodecyl phthalate series at 86° and a helium flow rate of 110 ml./min. Method 3 employed a 1-m. tris-2-cyanoethoxypropane column, 20% on 80/100 mesh firebrick, in series with a 2-m. diisodecyl phthalate

(36) R. F. Bridger, Ph.D. Dissertation, Iowa State University Library, Ames, Iowa, 1963.

(37) Prepared by Mr. R. S. Nicholson.

(38) The C–H frequency was absent in the infrared spectrum of the final product. The product of the previous treatment contained 6% hydrogen. Assumption that half of the remaining protium atoms were exchanged during the final treatment results in a value of 3% hydrogen.

(39) R. Renaud and L. C. Leitch, Can. J. Chem., **34**, 98 (1956).

(40) High resolution n.m.r. analysis performed by Dr. R. W. King.

(41) S. G. Cohen and C. H. Wang, J. Am. Chem. Soc., **75**, 5504 (1953).

(42) C. G. Overberger and A. V. DiGiulio, ibid., **80**, 6562 (1958).

(43) M. G. Alder and J. E. Leffler, ibid., **76**, 1425 (1954).

(44) A. Angeli, Atti accad. Lincei, [5] **19-1**, 793 (1910).

(45) C. Walling and E. S. Savas, J. Am. Chem. Soc., **82**, 1738 (1960).

(46) J. Bohemen, S. H. Langer, R. H. Perrett, and J. H. Purnell, J. Chem. Soc., 2444 (1960).

(47) S. H. Langer, C. Zahn, and G. Pantazopolos, J. Chromatog., **3**, 154 (1960).

TABLE VIII

RETENTION RATIOS

Compound	G.l.c. method	Retention ratio	Compound	G.l.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	sec-Butylbenzene	1	5.88
	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 chromotograms of standard solutions and conformed to the equation

moles A/area A = (moles B/area B) (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.

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

The Reactivity of Phenyl Radicals toward Molecular Oxygen[1]

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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 $R^+ {}^-O-O\cdot$.

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

$$2C_6H_5\cdot \longrightarrow C_6H_5-C_6H_5 \qquad (1a)$$

$$2C_6H_5OO\cdot \longrightarrow C_6H_5-C_6H_5 + 2O_2 \qquad (1b)$$
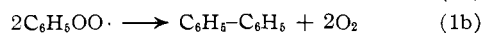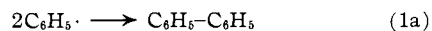
that the formation of biphenyl occurs via the intermediacy of phenylperoxy radicals. Numerous other examples suggest a low reactivity of oxygen toward

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

$$C_6H_5\cdot + O_2 \xrightarrow{k_O} C_6H_5OO\cdot \qquad (2)$$
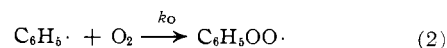
thermal decomposition of phenylazotriphenylmethane (PAT) at 60°, a process known to produce free phenyl radicals.[8]

$$C_6H_5\cdot + CCl_4 \xrightarrow{k_C} C_6H_5Cl + CCl_3\cdot \qquad (3)$$

$$C_6H_5\cdot + C_6H_{12} \xrightarrow{k_H} C_6H_6 + C_6H_{11}\cdot \qquad (4)$$

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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. Krieble 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_t for $2CH_3 \to C_2H_6$ is taken as 3.6×10^{-11} cc./molecule-sec. at 25° (A. Shepp, J. Chem. Phys., **24**, 939 (1956)), the termolecular reaction, $CH_3\cdot + O_2 + M \to CH_3O_2\cdot + M$, has a value of k_O of 1×10^{-31} (cc./molecule)^2 sec.$^{-1}$ at 25° where M is neopentane. At 100 mm. pressure of M, the pseudo-second-order value of k_O is 3.4×10^{-15} 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 $[CH_3]/[O_2]$ would have to be greater than 0.5×10^4 reacting, for 0.02 M oxygen the concentration of methyl radicals would have to exceed 1×10^{-4} M.

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

(6) R. T. Morrison, J. Cazes, N. Samkoff, and C. A. Howe, ibid., **84**, 4152 (1962).

(7) (a) G. A. Russell, ibid., **78**, 1044 (1956); (b) G. S. Hammond and U. S. Nandi, ibid., **83**, 1213 (1961).

(8) G. A. Russell and R. F. Bridger, Tetrahedron Letters, 737 (1963).