

fractionation in the course of the work-up procedure does not lead to significant errors in the product composition.

Quantitative Studies of the Chlorination of 1-Phenylpropene. The procedure followed was similar to that used for the 2-butenes. In a typical experiment, 0.8 g. of the 1-phenylpropene and 5 ml. of solvent were used. Temperatures for additions in carbon tetrachloride, methylene chloride, and methanol were maintained at 0–5° by the use of an ice–water bath, while temperatures for additions in acetic acid were kept at 22–25° with a water bath. The reaction was complete in 5 to 6 min. Samples were removed during this interval and either evaporated directly (carbon tetrachloride and methylene chloride as solvent) or dumped into water and extracted with pentane (acetic acid and methanol as solvent). In the latter case, the pentane layer was separated, washed with water, and dried over anhydrous potassium carbonate. The pentane was evaporated and the residue was analyzed by v.p.c. and, in many cases, by n.m.r. also. The v.p.c. and n.m.r. analyses were in good agreement. V.p.c. analyses were carried out with a 4 ft. \times $\frac{1}{8}$ in. column packed with 20% diethylene glycol succinate on Chromosorb P. The temperature was programmed from 75 at 1.5°/min., and the helium flow rate was 60 ml./min. The injection port temperature was maintained at 100° to avoid sample pyrolysis which occurred when higher temperatures were used. Retention times (in minutes) were: *cis*-1-phenylpropene, 4; *trans*-1-phenylpropene, 6.5; VI, 12; V, 14.5; XI, 18; XII, 20.5; I, 27; II, 29; and VII and VIII, 38. All of the samples obtained in acetic acid were analyzed by n.m.r. to obtain the ratio of VII to VIII.

To test the stability of the chlorination products in acidified methanol, a 0.7-g. sample containing I (58.7%), II (31.1%), V (1.6%), and VI (8.7%) was added to 5 ml. of 0.75 *M* methanolic hydrogen chloride

and the mixture was stirred at 0°. A 1-ml. sample was removed after 6 min. and worked up in the usual fashion. V.p.c. analysis showed the composition to be: I (59.5%), II (30.0%), V (1.6%), VI (8.8%),

Using known mixtures, it was demonstrated that no significant product fractionation occurs during the isolation process.

V.p.c. Procedure. Preparatory v.p.c. separations were carried out on an Aerograph Autoprep chromatograph using column A (10 ft. \times $\frac{3}{8}$ in.) or column B (4 ft. \times $\frac{3}{8}$ in.) packed with 30% diethylene glycol succinate on Chromosorb P. An Aerograph Moduline Model 202 chromatograph equipped with thermal conductivity detectors and a linear temperature programmer was used for the analytical measurements. The columns and conditions for the analytical separations have already been described. Peak areas were integrated with a disk integrator installed on the recorder, and mole ratios were taken equal to peak area ratios. The validity of this procedure was checked with known samples for the experiments with the 2-butenes and was verified by independent n.m.r. analyses for the experiments with the 1-phenylpropenes.

N.m.r. Procedure. N.m.r. spectra were measured on a Varian HR-60 spectrometer using the side-band technique to calibrate peak positions. Peak areas were integrated electronically. Samples were measured as approximately 15% v./v. solutions in carbon tetrachloride, containing tetramethylsilane as an internal standard.

Acknowledgment. We wish to express our appreciation to the National Science Foundation for a research grant (GP-2647) in support of this work, and also for a grant (GP-2137) assisting the purchase of the n.m.r. spectrometer used in these studies. We also wish to thank Dr. T. Tidwell of this department for a gift of *cis*-2-butene oxide.

Positive Halogen Compounds. XII.¹ Relative Reactivities of Hydrocarbons toward Alkoxy Radicals Determined by Direct and Indirect Methods²

Peter Wagner and Cheves Walling

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received February 25, 1965

Relative reactivities of hydrocarbons toward t-butoxy radicals derived from t-butyl hypochlorite have been determined in dilute chlorobenzene solution by direct competition and indirectly from t-butyl alcohol–acetone yields. For several pairs one of which contains benzylic hydrogen the results are inconsistent, indicating a more

complicated reaction path than previously assumed. It is shown that, in the cyclohexane–toluene system, the presence of toluene leads to increased yields of cyclohexyl chloride, although alcohol–acetone yields are additive. Results are consistent with a scheme in which attack on benzylic hydrogen occurs by two paths, one of which involves an unknown radical intermediate which can be intercepted by aliphatic hydrocarbons. A similar explanation is used to account for the enhanced reactivity of β -hydrogens in ethylbenzene and tetralin.

(1) Preceding paper in this series: C. Walling, L. Heaton, and D. D. Tanner, *J. Am. Chem. Soc.*, **87**, 1715 (1965).

(2) Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

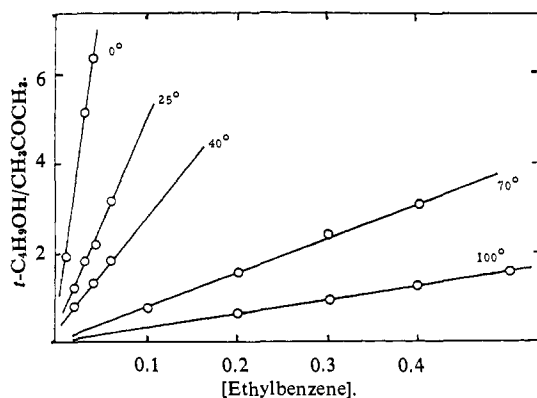
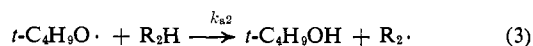
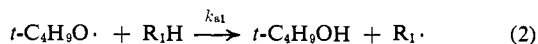
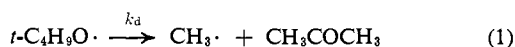
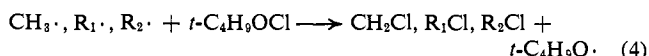


Figure 1. Alcohol/acetone ratios in *t*-butyl hypochlorite chlorination of ethylbenzene, 1:6 mole ratio in chlorobenzene.

Previous papers³ from this laboratory have demonstrated that tertiary alkyl hypochlorites, particularly *t*-butyl hypochlorite, are convenient radical halogenating agents and provide a very versatile method for studying the reactive properties of alkoxy radicals. The technique is particularly valuable since alkoxy radicals may be generated thermally or photochemically over a wide temperature range (at least from -78° to 100°) and since relatively simple products are produced *via* the various repeating competitive steps of long chain reactions. Thus, if one carries out the competitive chlorination of two hydrocarbon substrates, results heretofore have indicated that all significant products can be accounted for by the simple three-way competition for *t*-butoxy radicals



followed by



Since reactions 1–3 are all of the same order in *t*-butoxy radicals and are to a good approximation always followed by reaction 4 (assuming long chains) no knowledge of radical concentrations or over-all kinetics is required to interpret relative yields of products.

A question to which much of our earlier work has been addressed has been the problem of relative reactivities of different hydrocarbon substrates toward *t*-butoxy radical attack. In *t*-butyl hypochlorite reactions this has been obtained by *direct* competitive chlorination of two (or more) substrates *via* the relation

$$-d[\text{R}_1\text{H}]/-d[\text{R}_2\text{H}] = d[\text{R}_1\text{Cl}]/d[\text{R}_2\text{Cl}] = \frac{k_{a1}[\text{R}_1\text{H}]}{k_{a2}[\text{R}_2\text{H}]} \quad (5)$$

Alternatively, relative reactivities may be determined *indirectly*, a more convenient technique when *t*-butoxy radicals are generated in nonchain processes such as peroxide decompositions.⁴ Here *t*-butyl alcohol/ace-

(3) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960), and subsequent papers.

(4) For examples, *cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York N. Y., 1957, p. 470; also J. H. T. Brook and R. W. Glazebrook, *Trans. Faraday Soc.*, **65**, 1014 (1960).

tone ratios are determined separately in the presence of two substrates, and k_a/k_d ratios are determined *via*

$$d[\text{C}_4\text{H}_9\text{OH}]/d[\text{acetone}] = k_{a1}[\text{R}_1\text{H}]/k_d \quad (6a)$$

$$d[\text{C}_4\text{H}_9\text{OH}]/d[\text{acetone}] = k_{a2}[\text{R}_2\text{H}]/k_d \quad (6b)$$

whence

$$(k_{a1}/k_d)/(k_{a2}/k_d) = k_{a1}/k_{a2} \quad (7)$$

Recently⁵ we have shown that k_a/k_d ratios are strikingly solvent dependent and k_{a1}/k_{a2} ratios somewhat less so, a result which was interpreted in terms of extensive solvation of *t*-butoxy radicals and their transition states in the β -scission reaction (eq. 1), but some necessary loss of solvation in the hydrogen abstraction reactions 2 and 3. At the time we pointed out that the comparison of directly and indirectly measured reactivities would consequently be suspect if the reactions had been carried out in significantly different media.

In this paper we describe a comparison of direct and indirect reactivity measurements carried out at high dilution (under 0.5 *M*) for several substrates in chlorobenzene solution. Our results show some marked discrepancies and indicate that *t*-butoxy radical attack on benzylic hydrogen may occur by two different paths, one of which involves a transient intermediate other than the *t*-butoxy radical and interceptable by other substrates.

Results

k_a/k_d and $E_d - E_a$ Values for Selected Hydrocarbons. With chlorobenzene as solvent throughout, degassed (10^{-6} mm.) mixtures of *t*-butyl hypochlorite and hydrocarbon, usually in 1:5 mole ratio, with initial hydrocarbon concentrations ranging from 0.004 to 0.50 *M* (higher for *t*-butylbenzene), were photolyzed at 0, 25, 40, 70, and 100° , essentially as in our previous work.⁵ The resulting *t*-butyl alcohol/acetone ratios, as measured by gas-liquid partition chromatography (g.l.p.c.), were plotted against initial hydrocarbon concentrations. The slopes of the resulting straight lines equal k_a/k_d for each temperature. Figure 1 shows a typical set of results for ethylbenzene. Arrhenius plots of $\log k_a/k_d$ vs. $1/T$ gave good straight lines, and with the estimate from our previous work⁵ that E_d in chlorobenzene is 10.6 kcal./mole, it is possible to evaluate E_a for each hydrocarbon studied. All the data for these hydrocarbons are listed in Table I. It should be noted that the calculated Arrhenius parameters are reasonable, there being only slight differences in A_a values and the expected trend in E_a values. However, on both counts the numbers for toluene are anomalous.

Although Table I lists only ratios of rate constants, material balances were checked quantitatively with several systems, notably toluene, ethylbenzene, and cyclohexane. Yields of acetone + *t*-butyl alcohol were quantitative, and yields of chloride were 90–100% of those for *t*-butyl alcohol. It should be noted that some alcohol arises from attack on solvent as indicated by positive intercepts in plots similar to Figure 1, and to a lesser degree from small amounts of polychlorination of substrates. Neither reaction intro-

(5) C. Walling and P. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964).

Table I. Abstraction/Cleavage Ratios in Chlorobenzene for Various Hydrocarbons

Hydrocarbon	k_a/k_d^a at					$E_d - E_a^b$	E_a^c	Log ^d A/A_d	s_r^e
	100°	70°	40°	25°	0°				
Cyclopentene	9.21	31.5	122	235	1120	9.47	1.1	-5.17	±0.18
Cyclohexane	4.13	8.8	25.5	44.6	143	7.21	3.4	-4.71	0.11
2,3-Dimethylbutane	1.52	4.07	15.4	26.1	82.3	0.28
tertiary	1.24	3.48	13.9	23.9	77.4	8.43	2.2	-5.12	0.32
primary	0.28	0.59	1.5	2.2	4.9	5.82	4.8	-5.02	0.22
<i>t</i> -Butylbenzene	0.20	0.33	0.84	1.19	3.24	5.66	4.9	-5.00	0.21
Toluene	...	3.42	7.43	12.5	31.2	5.87	4.7	-3.68	0.08
Allylbenzene	2.65	5.97	26.6	57.6	187	8.90	1.7	-5.12	0.36
Ethylbenzene	3.35	8.00	26.3	48.3	148	0.14
α -isomer	3.02	7.43	25.3	46.8	146	7.93?	2.7?	-4.46?	0.14
Tetralin	17.8	60.2	163	357	1176	0.24
α -isomer	8.2	30.6	91	202	685	8.98	1.6	-4.91	0.36
Cyclopentane ^f			20.5						
<i>o</i> -Xylene ^f			22.5						

^a Per molecule, in l. mole⁻¹, corrected for thermal expansion of solvent. ^b Difference in activation energies, in kcal. mole⁻¹. ^c Assuming E_d in chlorobenzene equals 10.6 kcal. mole⁻¹. ^d Logarithm of the ratio of preexponential factors, per C-H bond. ^e Probable error (standard deviation) in $E_d - E_a$. ^f Values calculated from alkyl chloride/acetone ratios at a single concentration of hydrocarbon (0.050 M).

Table II. Relative Rates of *t*-Butoxy Radical Reactions with Ethylbenzene

	100°	70°	40°	25°	0°	$E_a - E_d$	Log A_d/A_a
α -Chloro, %	90.1	93.0	96.1	97.0	98.5	3.98 ^a	1.22 ^b
β -Chloro, %	9.0	7.0	3.9	3.0	1.5		
k_β/k_d	0.33	0.56	1.03	1.45	2.28	3.95	3.25
$C_6H_5C(CH_3)_3^c$	0.06	0.11	0.28	0.40	1.08	5.66	5.00
2,3-Dimethylbutane ^c	0.07	0.15	0.38	0.55	1.22	5.82	5.02

^b $E_\beta - E_\alpha$. ^a log A_β/A_α per H. ^c k_a/k_d values per CH_3 for comparison with k_β/k_d above.

duces serious errors into our measurements and the first is entirely corrected for by our method of treating data. Although quantum yields were not measured directly, our assumption of long chains also appears valid. Reactions were complete within a few hours' irradiation by a 140-w. ultraviolet lamp, and kinetic measurements of cyclohexane chlorination at similar concentrations using azobisisobutyronitrile initiator show chain lengths of at least 10^3 . No ring-chlorinated products were detected with aromatics, indicating the absence of competing polar reactions.

α/β Product Ratios. Isomer distributions in the chlorination of ethylbenzene and tetralin were determined by irradiating degassed solutions 0.01 M in *t*-butyl hypochlorite and 0.15 M in hydrocarbon at various temperatures, with chlorobenzene again the solvent. The products were analyzed by g.l.p.c., using low column and injector temperatures (100–110°). For both ethylbenzene and tetralin the ratio of α - β -chlorides from any one sample was reproducible to $\pm 2\%$ and total yields were essentially quantitative. These facts and the lack of any peaks corresponding to dehydrochlorination products indicate that no decomposition of the benzylic chlorides took place under the analytical conditions employed. Table II contains the observed product percentages for ethylbenzene and the k_β/k_d values calculated from them and the k_a/k_d values for the molecule as a whole in Table I (assuming $k_\alpha + k_\beta = k_a$). Included for comparison are the k_a/k_d values for one methyl group on *t*-butylbenzene and on 2,3-dimethylbutane. Table III lists the same data for tetralin and compares them to the analogous values for two methylenes on cyclohexane. The aliphatic β -hydrogens on these two compounds with α -benzylic positions apparently are 2–10 times more

reactive than comparable hydrogens both on purely aliphatic compounds and on aromatic compounds without any benzylic C-H bonds. Again the Arrhenius parameters for the β -positions do not appear normal.

Table III. Relative Rates of *t*-Butoxy Radical Reactions with Tetralin

	100°	70°	40°	25°	0°	$E_a - E_d$	A_d/A_a
α -Chloro, %	46.0	50.8	55.8	56.8	58.2		
β -Chloro, %	54.0	49.2	44.2	43.2	41.8	<i>a</i>	
k_β/k_d	9.6	29.6	72	155	491	7.92	4.24
Cyclohexane ^b	1.4	3.0	8.8	15.3	49	7.21	4.70

^a Data give curved Arrhenius plot. ^b k_a/k_d for two CH_2 groups (one-third of value per molecule).

Directly Measured Relative Reactivities. Various mixtures of the hydrocarbons in Table I were treated with *t*-butyl hypochlorite at 40° in chlorobenzene at a total concentration of reactants of 0.5 M or less. Measurement of the disappearance of each hydrocarbon relative to an inert internal standard was used to calculate values of relative reactivities in the usual manner.³ The results are listed in Table IV together with a comparison with corresponding indirectly measured values from Table I. Although the two methods give good agreement for purely aliphatic systems (and *o*-xylene-toluene), Table IV shows some striking discrepancies. These are most marked where aliphatic and benzylic compounds are compared where some aliphatic/benzylic ratios are 2–4 times higher by the direct method than by the indirect. Likewise the direct and indirect methods do not agree when comparing two

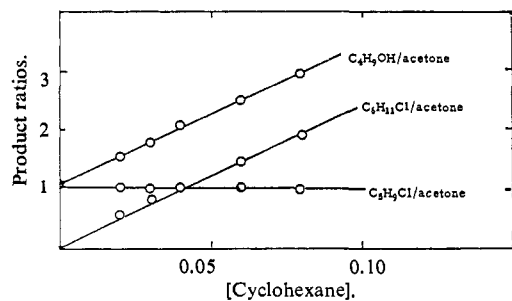


Figure 2. Effect of added cyclohexane on product ratios: 0.01 *M* *t*-butyl hypochlorite–0.05 *M* cyclopentane in chlorobenzene at 40°.

aromatic compounds if one or both have nonbenzylic C–H bonds, *i.e.*, ethylbenzene–tetralin. This behavior parallels the high reactivity of the aliphatic hydrogens on ethylbenzene and tetralin, molecules which have a built-in direct competition between aliphatic and benzylic C–H bonds.

Table IV. Direct and Indirect Relative Reactivities of Hydrocarbons in *t*-Butyl Hypochlorite Chlorination (40°, Chlorobenzene Solvent)

A	B	A/B		Direct/ indirect
		Indi- rect	Direct ^a	
Cyclohexane	Toluene	3.3	7.63 ± 0.03	2.3
<i>t</i> -Butylbenzene	Toluene	0.12	0.50 ± 0.03	4.1
Ethylbenzene	Toluene	3.5	2.67 ± 0.03	0.75
<i>o</i> -Xylene	Toluene	3.03	3.05 ± 0.05	1.0
Allylbenzene	PhEt	1.0	2.58 ± 0.06	2.6
Tetralin	PhEt	6.3	10.80 ± 0.60	1.8
Cyclopentene	Cyclohexane	4.9	6.1 ± 0.30	1.2
Cyclopentane	Cyclohexane	0.81	0.83 ± 0.03	1.0
2,3-Dimethyl- butane ^b	Cyclohexane	0.52 ^b	0.54 ± 0.03	1.0

^a Errors represent average deviation from mean of two or more runs. ^b Indirect value from calculated value of k_a/k_d at 40°, because the experimental value deviates from an otherwise straight Arrhenius plot.

Test for Deuterium–Hydrogen Exchange. Since exchange reactions could account for the above discrepancies, a 2:1 mixture of cumene- α - d_1 and *t*-butyl hypochlorite was photolyzed at 70°. N.m.r. analysis of the unreacted cumene showed that it had the same low percentage (about 2%) of α -H as the original deuterio-cumene. Mixtures of toluene- α - d_3 and hypochlorite in the presence of both cyclohexane and *t*-butylbenzene were also photolyzed at 70°. Both samples of unreacted toluene were subjected to mass spectrographic analysis at 15 v. The ratios of the 95/(94 + 93) *m/e* peaks were even larger than the value for the original deuterated toluene. Therefore what small change in deuterium content did occur must have resulted from a selective removal of the small amounts of PhCD₂H originally present.

Abstraction–Cleavage Measurements in the Presence of Two Reactive Substrates. Mixtures of two hydrocarbons in chlorobenzene were treated with *t*-butyl hypochlorite at 40°. The concentrations of one hydrocarbon (R_1H) and of hypochlorite (5:1 mole ratio) were kept constant while the concentration of the second hydrocarbon (R_2H) was varied. The resulting

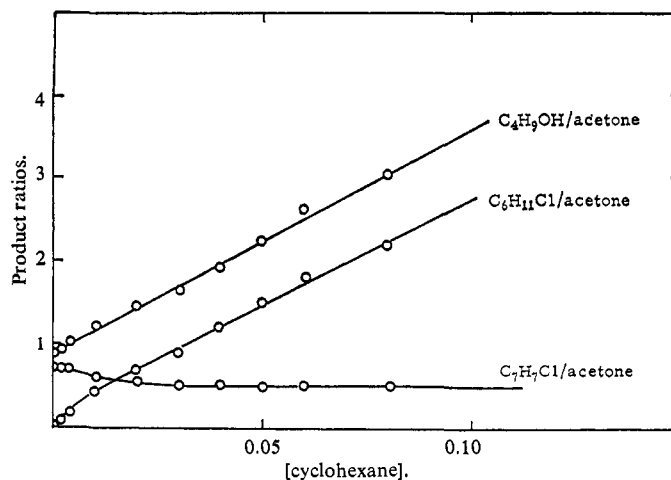


Figure 3. Effect of added cyclohexane on product ratios: 0.02 *M* *t*-butyl hypochlorite–0.10 *M* toluene in chlorobenzene at 40°.

amounts of alcohol, acetone, and alkyl chlorides were measured by g.l.p.c., using inert internal standards to calculate absolute yields. Ratios of alcohol and alkyl chlorides to acetone (all measures of k_a/k_d values) were then plotted against the initial concentration of the second hydrocarbon, with results shown in Figures 2, 3, and 4 and tabulated in Table V. Since these results are critical in our subsequent discussion it should be pointed out that while acetone and *t*-butyl alcohol yields are quantitative, the total yield of chlorides is less (85–95%) than that of alcohol because of some attack on solvent and possible polychlorination. No significant peaks corresponding to dichlorides were noted in the g.l.p.c. analysis and attack on solvent is a constant factor which does not affect our subsequent discussion. In fact, as pointed out in our earlier publication,⁵ the value of the *t*-butyl alcohol–acetone ratio at zero substrate concentration represents attack on solvent. In these mixed substrate experiments, the amount of attack on solvent is measured by the difference between the alcohol/acetone ratio and the R_1Cl /acetone ratio at zero R_2H concentration. In chlorobenzene at 40° this value averages 0.15 ± 0.05 . Since the solvent is 10 *M*, k_a/k_d for chlorobenzene then equals 0.015, so that chlorobenzene is approximately $1/1700$ as reactive as cyclohexane, in agreement with previous measurements.^{3,5}

Figure 2 demonstrates that addition of cyclohexane to fixed concentrations of cyclopentane does not affect the cyclopentyl chloride/acetone ratio, and that the presence of cyclopentane does not change k_a/k_d for cyclohexane as measured either by alcohol/acetone ratios or by cyclohexyl chloride/acetone ratios, the two yielding the same slope (24) in good agreement with Table I. Similar plots result upon adding *t*-butylbenzene to cyclopentane or toluene to *o*-xylene, and are, of course, precisely those expected from a mechanistic scheme involving reactions 1–3.

In contrast, addition of very small amounts of *t*-butylbenzene to *o*-xylene effects a sharp drop in the *o*-xylyl chloride/acetone ratio, the value of which levels off to about $2/3$ its initial value at concentrations of *t*-butylbenzene above 0.2 *M*. Figure 3 shows the same type of behavior in more detail: addition of cyclohexane to fixed concentrations of toluene–hypo-

Table V. Product Ratios in Reaction of *t*-Butyl Hypochlorite with Hydrocarbon Pairs in Chlorobenzene at 40°

R ₁ H	R ₂ H	Me ₃ COH/ Me ₂ CO	R ₁ Cl/ Me ₂ CO	R ₂ Cl/ Me ₂ CO
R ₁ H = cyclopentane, R ₂ H = cyclohexane				
0.050	0	1.05	1.01	0
0.050	0.020	1.54	1.00	0.53
0.050	0.030	1.78	0.97	0.80
0.050	0.040	2.07	1.01	1.02
0.050	0.060	2.47	1.01	1.44
0.050	0.080	2.93	0.96	1.86
R ₁ H = <i>o</i> -xylene, R ₂ H = toluene				
0.050	0	1.15	1.00	0
0.050	0.050	1.44	1.00	0.32
0.050	0.100	1.74	0.96	0.62
0.050	0.150	2.18	1.07	1.01
0.050	0.200	2.29	0.94	1.27
0.050	0.250	2.56	1.02	1.69
R ₁ H = cyclopentane, R ₂ H = <i>t</i> -butylbenzene				
0.050	0	1.13	1.10	^a
0.050	0.100	1.19	1.07	
0.050	0.200	1.24	1.09	
0.050	0.400	1.32	1.01	
0.050	0.600	1.43	0.98	
0.050	0.800	1.60	0.98	
R ₁ H = <i>o</i> -xylene, R ₂ H = <i>t</i> -butylbenzene				
0.050	0	1.35	1.20	^a
0.050	0.010	1.36	1.04	
0.050	0.200	1.46	0.80	
0.050	0.500	1.75	0.82	
0.050	0.800	1.82	0.78	
R ₁ H = cyclohexane, R ₂ H = toluene				
0.050	0	1.43	1.24	0
0.050	0.030	1.67	1.34	0.12
0.050	0.050	1.80	1.47	0.21
0.050	0.100	2.23	1.57	0.48
0.050	0.150	2.52	1.61	0.70
R ₁ H = toluene, R ₂ H = cyclohexane				
0.100	0	0.87	0.74	0
0.100	0.0020	0.92	0.71	0.08
0.100	0.0040	1.02	0.69	0.17
0.100	0.010	1.18	0.58	0.40
0.100	0.020	1.45	0.54	0.70
0.100	0.030	1.61	0.49	0.89
0.100	0.040	1.94	0.48	1.15
0.100	0.060	2.60	0.46	1.82
0.100	0.080	3.02	0.48	2.20

^a Absolute yield of PhC(CH₃)Cl not determined. However, plots of g.l.p.c. peak areas vs. acetone were linear with zero intercepts.

chlorite lowers the benzyl chloride/acetone ratio, again to about 2/3 its initial value at cyclohexane concentrations above 0.03 M. The slope of the cyclohexyl chloride/acetone plot goes up sharply while the benzyl chloride/acetone value is dropping, and after the benzyl chloride/acetone plot has leveled off assumes the same value as that of the slope of the alcohol/acetone plot which is linear throughout.

Figure 4 similarly depicts the effects of added toluene on the reactivity of cyclohexane. The cyclohexyl chloride/acetone ratio rises, while the alcohol/acetone slope is larger than the benzyl chloride/acetone slope. However, the sum of cyclohexyl and benzyl chlorides remains just slightly less than the amount of alcohol, so that the alcohol/acetone slope equals the sum of the values of the other two plus the same small constant value (0.15) resulting from attack on solvent. It should be pointed out that in Figure 3 the three slopes representing various abstraction/cleavage ratios be-

come constant at cyclohexane concentrations above one-fourth the toluene concentration. In Figure 4 the cyclohexane/toluene ratio is at least that large throughout. The numbers in Table V for the toluene-cyclohexane systems were reproduced three times with no more than 10% fluctuation in absolute values and absolutely no change in the shapes of Figures 3 and 4. Further, similar data have been obtained subsequently in our laboratory by another investigator.

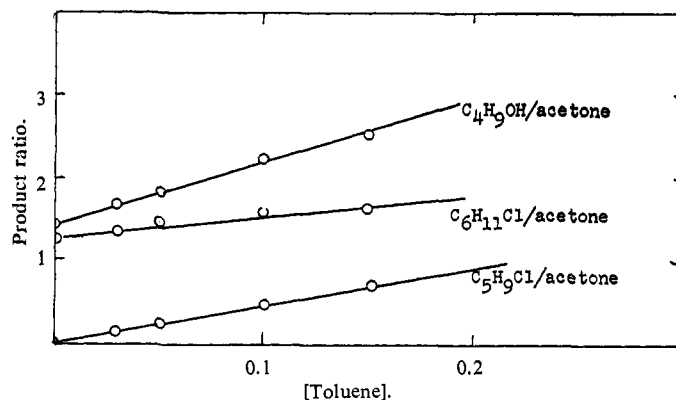


Figure 4. Effect of added toluene on product ratios: 0.01 M *t*-butyl hypochlorite-0.05 M cyclohexane in chloroform at 40°.

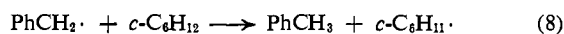
Discussion

The striking feature of our results is certainly the failure of direct and indirect methods to yield identical relative reactivities in systems involving benzylic and aliphatic C-H bonds (Table IV) and the indication that benzylic and aliphatic hydrocarbons somehow perturb each other's reactivity (Figures 3 and 4). Both findings are clearly inconsistent with the simple scheme, but they are not unprecedented. Previous work in this laboratory⁶ has shown that the direct-indirect relative reactivity relationship breaks down for alkoxy radicals undergoing facile β -scission (notably the radical from benzyl dimethylcarbinyl hypochlorite) in the presence of olefins. There, however, the phenomenon takes a different course since the olefin facilitates the β -scission process. We are convinced that both phenomena are real and important and that the whole problem needs further examination.

In sorting out the possible factors responsible for our results, it appears that here changes in k_d , the rate constant for the β -scission of the *t*-butoxy radical to acetone, are not responsible. Thus in Figures 2 and 3, alcohol/acetone plots are linear, and have the same slopes in mixed systems as when determined for toluene and cyclohexane individually. Accordingly, it appears that alcohol/acetone ratios are proper measures of the total amount of hydrogen available for abstraction in the system, and that whatever reactions cause aliphatic and benzylic hydrocarbons to alter the rates of formation of each other's chlorinated products must occur after the hydrogen abstraction step has become irrevocable and thus do not affect the formation of *t*-butyl alcohol.

A second possibility is ruled out by our deuterium-exchange experiments, and this is the exchange reaction

(6) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, 9, 1593 (1963).

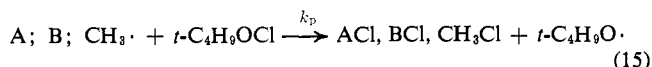
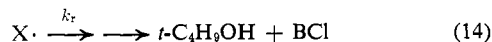
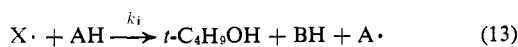
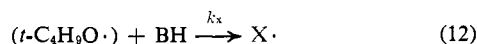
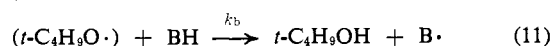
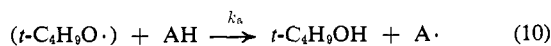


Such a process, besides being energetically implausible, would necessarily lead to deuterium exchange, and, as we have seen, none is observed between toluene- α - d_3 and either cyclohexane or *t*-butylbenzene, or between α - and β -positions of cumene- α - d_1 . The energetically favored reverse process has been demonstrated by Brook and Glazebrook⁴ under conditions of higher temperature and longer radical lifetimes (*t*-butyl peroxide decompositions at 135°). Although these workers suggest quite plausibly that it accounts for some discrepancies between "direct" and "indirect" relative reactivities which they observe, it could not account for our differences which are in the opposite direction.

Finally, inspection of Figure 3 shows that, while very small amounts of cyclohexane suppress the formation of benzyl chloride (which is replaced by an equivalent amount of cyclohexyl chloride), larger amounts have no further effect.

The conclusions which are forced on us, at least for the toluene-cyclohexane system, are that *t*-butoxy radical attack on toluene occurs by two paths. One, accounting for approximately $\frac{2}{3}$ of the reaction, is simple hydrogen abstraction which competes normally with β -scission and attack on cyclohexane. The second involves an unknown intermediate which normally goes on to benzyl chloride, but may be intercepted by cyclohexane to yield cyclohexyl chloride instead.

Our observations and these conclusions can be expressed in terms of the following modified reaction sequence which fits the data but admittedly raises a number of questions which can only be answered by further work.



where (*t*-C₄H₉O·) represents the *t*-butoxy radical solvated by chlorobenzene, AH and BH, hydrocarbons with aliphatic and benzylic C-H bonds, and X· the "phantom intermediate." Here reactions 9-11 indicate a normal competition, but BH also reacts with the *t*-butoxy radical via reaction 12 to yield X· which, if not intercepted by AH (reaction 13), goes on to yield benzyl chloride via reaction 14. For the time being, reaction 14 is simply indicated as a pseudo-first-order reaction of unknown nature. However, the linear nature of alcohol/acetone plots mentioned above indicates that X· is *not* formed reversibly and does not itself decompose to acetone to any measurable extent.

This modified mechanism predicts the following equations for the various abstraction cleavage competitions.

$$[t\text{-C}_4\text{H}_9\text{OH}]/[\text{acetone}] = (k_a[\text{AH}] + k_b[\text{BH}] + k_x[\text{BH}] + k_s[\text{S}])/k_d \quad (16)$$

where k_s represents the rate constant for any abstraction from the chlorobenzene solvent.

$$[\text{ACl}]/[\text{acetone}] = (k_a[\text{AH}]/k_d) + k_x[\text{BH}]k_i[\text{AH}]/k_d(k_i[\text{AH}] + k_r) \quad (17a)$$

$$[\text{BCl}]/[\text{acetone}] = (k_b[\text{BH}]/k_d) + k_x[\text{BH}]k_r/k_d(k_i[\text{AH}] + k_r) \quad (17b)$$

With AH or BH alone reaction 17 reduces to

$$[\text{ACl}]/[\text{acetone}] = k_a[\text{AH}]/k_d \quad (18a)$$

$$[\text{BCl}]/[\text{acetone}] = (k_b + k_x)[\text{BH}]/k_d \quad (18b)$$

while, at high cyclohexane concentrations where $k_i[\text{AH}] \gg k_r$

$$[\text{ACl}]/[\text{acetone}] = (k_a[\text{AH}] + k_x[\text{BH}])/k_d \quad (19a)$$

$$[\text{BCl}]/[\text{acetone}] = k_b[\text{BH}]/k_d \quad (19b)$$

Using the data at these limiting conditions, $k_a/k_d = 25.5$, $k_b/k_d = 4.8$, and $k_x/k_d = 2.6$. From low cyclohexane data in Table V, $k_i/k_r \approx 140$. The solid lines in Figures 3 and 4 are drawn using these values and illustrate the extent to which the data are accommodated.⁷

From our scheme, indirect reactivity measurements give actually $k_a/(k_b + k_x)$, the ratio of total reactivities. Direct measurements involve a complex relationship which approximates

$$[\text{ACl}]/[\text{BCl}] = k_a[\text{AH}]/k_b[\text{BH}] \quad (20)$$

at high [AH]/[BH] ratios; but as [AH]/[BH] goes below unity (a quite normal experimental situation), the importance of other terms increases. Thus, direct competition experiments may give relative reactivities dependent on the ratio of substrates, and it is evident why the two methods fail to agree.

Although the phantom intermediate X· is required by our analysis, its structure and reactions are certainly peculiar. The simplest hypothesis is that it represents some sort of toluene-*t*-butoxy radical complex which rearranges to *t*-butyl alcohol and a benzylic radical



If so, it differs markedly from the *t*-butoxy radical solvated by chlorobenzene, since it appears to be formed irreversibly and requires the presence of a benzylic hydrogen (thus *t*-butylbenzene behaves normally in both direct and indirect comparisons; cf. Tables I and V). Further, it shows quite different selectivity. Thus the solvated *t*-butoxy radical in the presence of 0.05 *M* cyclohexane and 0.05 *M* toluene undergoes β -scission and attack on cyclohexane and toluene at relative rates of 1:1.3:0.24. In contrast X· shows reaction only with cyclohexane at this concentration and undergoes no β -scission. There is also evidence that X· shows a modified selectivity for different types of

(7) In systems containing very small amounts of cyclohexane a significant fraction (up to 50%) of it was consumed. Accordingly average concentrations, obtained from the data of Table V, were used in the calculation. Actually, in the conventional scheme this depletion should have made the cyclohexyl chloride/acetone plot of Figure 4 concave upward.

aliphatic hydrogen. Table VI lists relative reactivities of tertiary and primary hydrogens of 2,3-dimethylbutane in a series of aromatic solvents. Although actual selectivity differences are small, the Arrhenius parameters for solvent toluene are clearly different from those of similar solvents, and 1 M solutions of toluene in chlorobenzene give the same result as pure toluene.

Table VI. Effect of Aromatic Solvents on k_t/k_p in *t*-Butyl Hypochlorite Chlorination of 2,3-Dimethylbutane^a

Solvent	70°	40°	25°	0°	$E_p - E_t$	Log A_t/A_p
C ₆ H ₅ CH ₃	30	48	62	96	3060	-0.45
C ₆ H ₅ OCH ₃	45	65	72	106	2250	+0.22
C ₆ H ₅ C(CH ₃) ₃	44	63	75	96	2050	+0.35
Benzene	...	55	...	89	1990	+0.35
C ₆ H ₅ Cl	35	54	66	94	2580	-0.08
1 M PhCH ₃ in PhCl	29	46	63	93	3090	-0.49
None	...	44	...	68	1850	+0.35

^a Data except for toluene systems from ref. 5.

Although we have not investigated other systems in detail, we assume that the same sort of dual path for benzylic hydrogen abstraction accounts for the other inconsistencies between directly and indirectly measured relative reactivities in Table IV.

Our scheme also suggests an explanation for the surprisingly high reactivities of β -hydrogens in ethylbenzene and tetralin (Tables II and III) since here β -substitution can occur either by direct attack or by the quenching of an X· type intermediate by another hydrocarbon molecule. For ethylbenzene, k_β/k_α is twice as large at 0° as would be anticipated by comparison with *t*-butylbenzene and 2,3-dimethylbutane and becomes five times as large at 100°, a result suggesting that the amount of β -chloride formed through our phantom intermediate increases from 50 to over 80% as the temperature is raised from 0 to 100°. The tetralin case⁸ is even more striking since α - and β -positions are of almost equal reactivity. Here k_β/k_α is roughly ten times that anticipated from cyclohexane, implying 90% of the reaction at the β -position *via* an X· species.

If our conclusions are correct, it is evident that much of the data on relative reactivities of hydrocarbons toward alkoxy (and perhaps other) radicals are of only qualitative significance, and good Arrhenius plots for reactions involving benzylic hydrogen (e.g., toluene in Table I) are perhaps fortuitous and yield activation parameters of uncertain significance. Further kinetic and product studies to establish the nature and generality of "phantom intermediates" in alkoxy radical reactions are in progress, but since

(8) Unusual reactivity of tetralin has been noted in other radical reactions, and J. A. Meyer, V. Stannett, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 25 (1961), have suggested a conformational explanation leading to higher α -reactivity. Here, however, the increase occurs in the β -position.

results will not soon be available, and since we believe that our measurements are both reliable and reproducible, we report the status of our investigation at this time.

We have reported all of our present results on hydrocarbon reactivities in Table I, even though all are not completely relevant to the main issue of this paper, primarily to emphasize the abnormal behavior of a few (toluene, ethylbenzene, and tetralin). Our over-all results indicate that the tabulated reactivities of the aliphatic compounds are very accurate, and consistent with expectation. However, the behavior of allylbenzene deserves comment for two reasons. First is the interesting crossing of the Arrhenius plots (Table I) for it and ethylbenzene, so that the anticipated lower activation energy for hydrogen abstraction from an allylic C-H bond is not readily apparent from a simple comparison of their relative reactivities. Second, although the available hydrogens in allylbenzene are benzylic, its activation parameters are normal and its reactivity is apparently enhanced in the presence of ethylbenzene.

Experimental Section

All determinations of k_a/k_d ratios and relative reactivities were carried out essentially as described previously, employing g.l.p.c. with a flame ionization detector (Wilkens Instrument Co. Hi-Fi 600) for analyses. Alcohol/acetone ratios were determined on a 10-ft. 15% Carbowax 20 M column. Mixed substrate reactions were analyzed using internal standards and the same column or one packed with 5% QF-1:1% Carbowax 20 M. Reaction products from tetralin and ethylbenzene were analyzed on the latter column at a temperature of 110–120° to avoid pyrolysis.

Reactions of deuterio compounds were carried out as follows. Deuteriocumene was prepared by treating α -chlorocumene with zinc and deuterioacetic acid in ether⁹ and collected by preparative g.l.p.c. after removal of solvent. Its n.m.r. spectrum showed approximately 2% α -hydrogen. One gram was treated with 0.4 g. of *t*-butyl hypochlorite by irradiating at 70° in a sealed degassed tube. Unreacted cumene was separated by preparative g.l.p.c. and showed an n.m.r. spectrum identical with starting material. Toluene- α -*d*₃ was obtained from Merck and Co. Ltd. One sample (11.4 mmole) was treated with 4.3 mmoles of cyclohexane and 5.0 mmoles of *t*-butyl hypochlorite at 70°. Another (8.0 mmoles) was treated similarly with 7.8 mmoles of *t*-butylbenzene and 4.3 mmoles of hypochlorite. Unreacted toluene was separated from each product by preparative g.l.p.c. (Carbowax 20 M column) and subjected to mass spectrographic analysis at 15 v.¹⁰ No increase in hydrogen was detected, and samples actually showed a small deuterium enrichment.

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

(10) We are indebted to Mr. Al Struck of Perkin Elmer, Inc., Norwalk, Conn. for the analysis.