[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Competitive Halogenation of Cyclohexane and Aralkyl Hydrocarbons; Evidence as to the Nature of the Transition States in Halogenation Reactions[1,2]

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The competitive photohalogenation of cyclohexane and toluene at 80° revealed that toluene is 60 times as reactive as cyclohexane toward bromine atoms, whereas toward chlorine atoms cyclohexane is 11 times as reactive as toluene. This surprising greater reactivity of cyclohexane in chlorination was verified by competitively chlorinating both toluene and cyclohexane in the presence of cumene as the reference compound. The great difference in the photobromination and photochlorination results is attributed to the difference in the nature of the transition states in the two reactions. It is proposed that in photobromination the transition state involves a large measure of carbon–hydrogen bond breaking, so that the resonance stabilization of the incipient benzyl free radical contributes to the higher reactivity of toluene. On the other hand, it is believed that in the transition state of the chlorination reaction, the carbon–hydrogen bond is but slightly broken. Consequently the resonance stabilization of the incipient free radical contributes but little to the ease of rupture of the primary carbon–hydrogen bond. It is concluded that in order to account for the effect of structure on the selective rates of free radical reactions involving carbon–hydrogen bonds it is necessary to consider (1) bond dissociation energies, (2) the extent of bond-breaking in the transition state, and (3) polar effects both in the molecule being attacked and in the attacking species.

It has been generally assumed that the selectivity displayed by a free radical or atom in attack upon a system of carbon–hydrogen bonds is determined by the relative bond dissociation energies of these bonds,[3] and by the reactivity of the attacking atom or radical. Thus the photohalogenation of branched-chain hydrocarbons has shown that the reactivities of the hydrogen atoms are in the same order as the bond dissociation energies of the carbon–hydrogen bonds[3,4] and that bromine atoms are more selective than the more reactive chlorine atoms in attack upon branched-chain hydrocarbons.[5]

However, a number of examples of aliphatic substitutions have been reported that do not appear to be in agreement with this general rule. Among the more outstanding cases of this kind are the predominantly β-attack of isobutyric acid in chlorination[6] as compared to predominant α-attack of the molecule by methyl and/or acetoxyl radicals formed in the decomposition of acetyl peroxide,[7] and the predominantly α-bromination but β-chlorination of pentachloroethylbenzene.[8]

Furthermore, it has been observed that the halogen atoms of alkyl halides deactivate the neighboring hydrogen atoms to attack by chlorine atoms,[4,6b,9] while toward alkyl radicals the reactivity of hydrogen is markedly increased by the presence of chlorine atoms on the same carbon atom.[10,11]

Finally, H. C. McBay and his co-workers have shown that methyl radicals generated by the decomposition of acetyl peroxide preferentially attack the tertiary hydrogen atom of the dichloromethyl group in *p*-isopropylbenzal chloride, whereas ethoxyl radicals generated by the decomposition of diethylperoxydicarbonate preferentially attack the hydrogen atom, not of the dichloromethyl, but of the isopropyl group.[12]

It should be noted that strongly polar groups are present in the molecule in all cases where such a reversal in selectivity has been observed. It appeared probable, therefore, that the competitive halogenation of a variety of aliphatic and aralkyl hydrocarbons should provide reliable data to test the hypothesis that reactivity is a function of bond strength. However, it soon was observed that even in such relatively non-polar materials as toluene and cyclohexane the relative reactivity may be greatly altered and, indeed, actually inverted by a change in the nature of the attacking species. Accordingly, major emphasis was devoted to a study of this phenomenon.

Results

Mixtures of toluene and cyclohexane were com-

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[1] Directive Effects in Aliphatic Substitutions. V.

[2] This paper is abstracted from a thesis submitted by Glen A. Russell in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938); E. C. Baughan and M. Polanyi, *Nature*, **146**, 685 (1940); E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943); E. Warhurst, *Quart. Revs. (London)*, **5**, 44 (1951); M. G. Evans, *Disc. Faraday Soc.*, **2**, 271 (1947). It has been suggested that a linear relationship, $\Delta E_a = \alpha\Delta H$ or $\Delta E_a = \alpha\Delta H +$ constant, should exist between the energy of activation and the heat of reaction (and thus the bond dissociation energy of the bond which is being broken) for reactions of the type $AB + C\cdot \rightarrow A\cdot + BC$, involving equal amounts of resonance stabilization of the transition state. The validity of this relationship is supported by data for the attack on aliphatic hydrocarbons of chlorine atoms, peroxy radicals and methyl radicals; H. Steiner and H. R. Watson, *ibid.*, **2**, 88 (1947); J. L. Bolland, *Quart. Revs. (London)*, **3**, 1 (1949); A. F. Trotman-Dickenson, *ibid.*, **7**, 198 (1953).

[4] H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, **28**, 333 (1936).

[5] G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4025 (1955).

[6] (a) M. S. Kharasch and H. C. Brown, *ibid.*, **62**, 925 (1940); A. Michael, *Ber.*, **34**, 4028 (1901); (b) A. B. Ash and H. C. Brown, *Record of Chemical Progress*, **9**, 81 (1948); (c) A. Bruylants, M. Tits and R. Darby, *Bull. soc. chim. Belges*, **58**, 310 (1949); A. Bruylants, M. Tits, C. Dieu and R. Gauther, *ibid.*, **61**, 301 (1952).

[7] (a) M. S. Kharasch and M. T. Gladstone, THIS JOURNAL, **65**, 15 (1943); (b) C. C. Price and H. Morita, *ibid.*, **75**, 3686 (1953).

[8] S. D. Ross, M. Markarian and M. Nazzewski, *ibid.*, **69**, 1914, 2468 (1949).

[9] D. V. Tishchenko and A. Churbakov, *J. Gen. Chem. (U.S.S.R.)*, **7**, 658, 897 (1937); *C. A.*, **31**, 5755 (1937); M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939); H. C. Brown and A. B. Ash, *ibid.*, **77**, 4019 (1955); W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, **5**, 449 (1940); F. F. Rust and W. E. Vaughan, *ibid.*, **6**, 479 (1941). See also publications by A. L. Henne and co-workers, THIS JOURNAL, **64**, 1157 (1942); **67**, 1194, 1197 (1945).

[10] M. S. Kharasch and G. Buchi, *ibid.*, **73**, 632 (1951).

[11] The bond dissociation energies of the carbon–hydrogen bonds in methane, methyl bromide, methylene bromide and bromoform are 102, 99, 96 and 95 kcal./mole, respectively. It therefore appears that the substitution of a halogen atom for one or more of the hydrogen atoms of a methyl group lowers the bond dissociation energy of the remaining carbon–hydrogen bonds of the methyl group; H. G. Andersen, G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, **10**, 305 (1942); J. H. Sullivan and N. Davidson, *ibid.*, **19**, 143 (1951).

[12] H. C. McBay, O. Tucker and P. T. Groves, Abstracts of Papers, 126th Meeting of the American Chemical Society, New York, N. Y., Sept., 1954, p. 75-O.

TABLE I

THE COMPETITIVE HALOGENATION OF CYCLOHEXANE AND TOLUENE[a]

Temp., °C.	80	80	80	80	80	80	55	0–2
Reactants								
Cyclohexane	1.486	1.925	0.855	0.789	0.604	0.340	0.325	0.237
Toluene	0.536	1.940	2.610	2.423	1.845	1.068	1.115	1.145
Sulfuryl chloride[b]		0.52	0.29					
Chlorine				0.29	0.18	0.12	0.10	0.10
Bromine	0.19							
Products								
Hydrogen chloride						0.113	0.096	0.086
Alkyl halides	0.190	0.497	0.286	0.285	0.174	.114	.105	.112
Benzyl halide	.179	.040	.060	.068	.043	.027	.022	.0318
Halocyclohexane[c]	.011	.457	.226	.217	.131	.087	.083	
Cyclohexane[d]	1.383	1.361	.625	.570	.443	.239	.232	
Toluene[d]	0.320	1.857	2.548	2.354	1.790	1.038	1.090	
Mole % halogenation	9.4	13.9	8.3	8.9	7.1	8.6	6.9	7.3
Mean cyclohexane–toluene ratio	3.55	0.863	0.287	0.280	0.288	0.275	0.251	
Reactivity of cyclohexane[e]	0.017	13.2	13.1	11.4	10.6	11.7	15.0	

[a] All quantities in moles. [b] 1% by weight of benzoyl peroxide added. [c] By difference. [d] Initial quantity minus amount substituted and amount vaporized. [e] Reactivity of toluene assumed to be 1.00.

petitively photobrominated, photochlorinated and sulfuryl chloride chlorinated at 80° in order to obtain the relative reactivities of the two hydrocarbons. The reaction mixtures were analyzed for total halide and for benzyl halide (by selective reaction with piperidine). The results of the chlorination experiments also were checked in several instances by careful fractionation and isolation of the products.

The chlorine or bromine was introduced into the mixture of hydrocarbons in a stream of nitrogen. The halogenations were performed only to the extent of about 10 mole % and dihalide formation has been assumed to be negligible. At 80° it was observed that one mole of chlorine produces one mole of alkyl halide and one mole of hydrogen chloride. It therefore appears that addition of chlorine to the aromatic ring is not important at this temperature. At 55° the agreement was less satisfactory, while at 0–2° it appeared that considerably more alkyl chloride and less hydrogen chloride were formed than corresponded to the chlorine added.[13]

In photobromination the results indicated that toluene was 60 times as reactive as cyclohexane. This was in accord with expectations in view of the low bond dissociation energy of the benzyl–hydrogen bond.[14] However, in photochlorination the results showed cyclohexane to be more reactive than toluene 11.2:1.00. Similar results were obtained in sulfuryl chloride chlorination—cyclohexane: toluene = 13.1:1.00. The higher ratio in this case corresponds to the greater selectivity of sulfuryl chloride chlorination noted previously.[15]

These results were checked repeatedly. The conclusion appears to be unavoidable that in bromination each carbon–hydrogen bond of toluene is more reactive than the corresponding bond of cyclohexane, whereas in chlorination the reverse is true.

The experimental data are summarized in Table I.

To provide an independent measure of the relative reactivity of cyclohexane and toluene, it was decided to photochlorinate each of these substances against a third hydrocarbon. Cumene was selected as a convenient reference compound, since the rapid solvolysis of 2-chloro-2-phenylpropane provided a convenient analytical procedure for this product in the presence of chlorocyclohexane and benzyl chloride. From the amount of 2-chloro-2-phenylpropane formed and a knowledge of the distribution of the isomers produced in the chlorina-

TABLE II

THE COMPETITIVE PHOTOCHLORINATION OF CYCLOHEXANE AND TOLUENE WITH CUMENE AT 80°[a]

Reactants			
Cumene	0.700	0.446	0.352
Toluene	.562		
Cyclohexane		.323	.348
Chlorine	.090	.046	.046
Products			
Alkyl chlorides	.0896	.0465	.0479
2-Chloro-2-phenylpropane	.0359	.0064	.0055
1-Chloro-2-phenylpropane[b]	.0169	.0030	.0026
Benzyl chloride	.0368		
Chlorocyclohexane[c]		.0371	.0398
Cumene	.647	.473	.344
Toluene	.525		
Cyclohexane[d]		.283	.260
Mole % chlorination	7.1	6.0	6.6
Mean hydrocarbon–cumene ratio	0.807	0.662	0.872
Reactivity of toluene	1.00[e]		
Reactivity of cumene	1.96	1.96[e]	1.96[e]
Reactivity of cyclohexane		11.7	11.1

[a] All quantities in moles. [b] (6/12.8) 2-chloro-2-phenylpropane.[15] [c] By difference. [d] Initial quantity minus amount substituted and amount vaporized. [e] Assumed.

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[13] These results are in agreement with observations that the free radical halogenation of toluene gives only the benzyl halide at elevated temperatures, but a mixture of benzyl halide and ring addition products at low temperatures; M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939); J. R. Sampey, F. S. Fawcett and B. A. Morehead, *ibid.*, **62**, 1839 (1940); M. S. Kharasch and M. G. Berkman, *J. Org. Chem.*, **6**, 810 (1941).

[14] M. S. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

[15] H. C. Brown and G. A. Russell, THIS JOURNAL, **77**, 4031 (1955).

tion of cumene,[15] the amount of 1-chloro-2-phenylpropane formed can be calculated. It is now possible from an analysis of the total alkyl halide to calculate toluene–cumene and cyclohexane–cumene reactivity ratios.

Assigning toluene a reactivity of 1.00, the cumene reactivity is 1.96, and the cyclohexane reactivity is 11.4. The cyclohexane–toluene reactivity ratio therefore agrees closely with the value determined in the direct comparison.

The experimental data are summarized in Table II.

We also photochlorinated cumene and toluene *versus* *t*-butylbenzene, taking advantage of the inertness of neophyl chloride to analyze for 2-chloro-2-phenylpropane and for benzyl chloride by the methods previously mentioned. The results of these chlorinations are summarized in Table III.

TABLE III

THE COMPETITIVE PHOTOCHLORINATION OF TOLUENE AND CUMENE WITH *t*-BUTYLBENZENE AT 80°[a]

Reactants				
t-Butylbenzene	0.694	0.665	0.413	0.410
Cumene			.486	.322
Toluene	.702	.854		
Chlorine	.106	.111	.052	.046
Products				
Alkyl chlorides	.1058	.1127	.0552	.0464
2-Chloro-2-phenylpropane			.0303	.0229
1-Chloro-2-phenylpropane[b]			.0143	.0107
Benzyl chloride	.0631	.0775		
Neophyl chloride[c]	.0427	.0378	.0106	.0128
t-Butylbenzene	.617	.627	.404	.397
Cumene			.441	.289
Toluene	.643	.777		
Mole % chlorination	7.8	7.1	6.1	6.3
Mean hydrocarbon–*t*-butylbenzene ratio	0.946	0.794	0.892	1.322
Reactivity of toluene	1.00[d]	1.00[d]		
Reactivity of *t*-butylbenzene	0.72	0.63	0.68[d,e]	0.68[d,e]
Reactivity of cumene			2.46	2.36

[a] All quantities in moles. [b] (6/12.8) 2-chloro-2-phenylpropane.[15] [c] By difference. [d] Assumed. [e] Average of 0.72 and 0.63.

The relative reactivity of cumene to toluene of 2.42:1.00 determined in these experiments is in fair agreement with the values of 1.96:1.00 observed in the direct competitive chlorination of cumene and toluene and 2.04:1.00 observed with cyclohexane as the reference compound. The latter two values probably are to be preferred because of the tendency of *t*-butylbenzene to undergo addition of chlorine to the aromatic ring.[16]

Discussion

The relative reactivities obtained by the competitive photochlorination of toluene, cumene and *t*-butylbenzene form a series of reactivities consistent with bond dissociation energies. Moreover, the relative reactivities of these hydrocarbons as measured by the photochlorination technique agree closely with the relative tendencies of these hydrocarbons to undergo reaction with the styrene polymer radical,[17] with the trichloromethyl radical,[18] and with the methyl and/or acetoxy radical from acetyl peroxide.[19]

From the reactivities of the alkyl benzenes given in Table IV, it appears that the selectivity of removal of a hydrogen atom is in the order: chlorine atom < methyl radical < trichloromethyl radical < styrene polymer radical. The bond energies of hydrogen chloride, methane, chloroform and toluene decrease in the same order. Thus there appears to be a direct correlation between the strength of the new bond being formed and the reactivity of the attacking species. The stronger the new bond, the more reactive the attacking species (chlorine atom > methyl radical > trichloromethyl radical > styrene polymer radical), and the lower its selectivity.

Consideration of the cyclohexane results reveals a difficulty with this simple picture. Toluene has a much lower bond dissociation energy than cyclohexane—the latter therefore should be much less reactive than toluene on the basis of the arguments presented. Yet the results reveal that in photochlorination at 80° a cyclohexane hydrogen atom is 2.8 times as reactive as a toluene side-chain hydrogen atom.

On the other hand, photobromination gives a complete reversal of selectivity; a cyclohexane hydrogen atom is only 0.004 as reactive as a toluene hydrogen atom. Moreover, styrene polymer radicals and methyl and/or acetoxy radicals give relative reactivities similar to that observed in bromination.

We examined and discarded the possibilities that the unexpected results in chlorination might be the result of a loss of benzyl free radicals through dimerization, or of an exchange reaction of benzyl free radicals with cyclohexane,[20] or of some unusual differences in the energies of activation and frequency terms in the two reactions.[21]

It therefore appears that unusual directive effects and reversals in directive effects exist in the free radical substitution reactions of hydrocarbons as well as in those of their strongly polar derivatives.[6–8] In fact, it seems possible that the same forces that cause the anomalous relative reactivities previously mentioned for aliphatic acids,[6,7] pentachloroethylbenzene[8] and alkyl halides[6b,9,10] may be

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[16] J. Salibill, *Bull. intern. acad. sci. Cracovie*, [A] 606 (1910); *C. A.*, **5**, 2822 (1911); W. E. Truce, E. T. McBee and C. C. Alfieri, THIS JOURNAL, **72**, 2740 (1950).

[17] R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947).

[18] E. C. Kooyman, *ibid.*, **10**, 163 (1951).

[19] W. H. Urry, Abstracts of Papers, 12th National Organic Chemistry Symposium, Denver, Colo., June, 1950, p. 30. See also F. G. Edwards and F. R. Mayo, THIS JOURNAL, **72**, 1265 (1950).

[20] This possibility could be excluded on the basis of chlorination results with α-d_1-toluene as a reference hydrocarbon; H. C. Brown and G. A. Russell, *ibid.*, **74**, 3995 (1952).

[21] Since the relative reactivity of two carbon–hydrogen bonds may be expressed as rel. react. $= k_1/k_2 = A_1/A_2 \exp (E_{a_1} - E_{a_2})/RT$, it appeared possible that the unusual chlorination results might be controlled primarily by the frequency term, with the bromination results depending primarily upon differences in the activation energies and therefore upon differences in the bond energies. However, the difference in the relative reactivity of cyclohexane and toluene at 55° and 80° (Table I) must mean that the energy of activation term favors the attack of the chlorine atom on a cyclohexane in preference to a toluene hydrogen atom.

TABLE IV

RELATIVE REACTIVITIES OF HYDROCARBONS ON A MOLECULAR AND BOND BASIS

Hydrocarbon	Chlorine atom 80°		Styrene radical 60°[a,17]		Trichloromethyl radical 91.5°[18]		Acetyl peroxide decomposition[19]	
	Molec.[d]	Bond[e]	Molec.[d]	Bond[e]	Molec.[d]	Bond[e]	Molec.[d]	Bond[e]
t-Butylbenzene	0.67	0.22	0.48	0.16	0.24	0.08		
Toluene	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Cumene	2.00		6.6		4.16		3.2	
tert. hydrogen		4.0		18.9		12.0		9.7[c]
prim. hydrogen		0.31		0.16[b]		0.08[b]		
Cyclohexane	11.2	2.8	0.19	0.05			1.20	0.30

[a] Assuming all chain transfer to be due to the abstraction of a side-chain hydrogen atom. [b] Assumed to be equal to a hydrogen atom of *t*-butylbenzene. [c] Neglecting the contribution of the primary hydrogen atoms. [d] Reactivity per molecule. [e] Reactivity per carbon–hydrogen bond.

responsible for the phenomena observed in the competitive substitution reactions of toluene and cyclohexane.

We propose that the marked difference in the relative reactivity of toluene and cyclohexane in bromination and chlorination is due to a marked difference in the degree of bond-breaking in the respective transition states.

In the reaction with chlorine the transition state evidently involves only a small degree of bond-breaking in the carbon–hydrogen bond. In a previous paper we have argued that the carbon–hydrogen bond is broken only to the extent of approximately 10% in the transition state of the chlorination reaction.[15]

On the other hand, in attack by methyl free radicals, the evidence is that the carbon–hydrogen bonds are more extensively broken, in the neighborhood of 50%.[22] It is suggested that in the transition state in the bromination reaction, the carbon–hydrogen bond is also extensively broken.

In chlorination, with the carbon–hydrogen bond only slightly broken, there will be little resonance stabilization of the incipient benzyl free radical and such stabilization is therefore, unable to contribute much to stabilization of the transition state. On the other hand, in bromination, with the carbon–hydrogen bond being extensively broken in the transition state, resonance stabilization could contribute a great deal to the reaction.

In other words, according to this proposal the actual reactivities of the α-carbon–hydrogen bonds in toluene will vary markedly with the activity of the attacking species and the varying degrees of stabilization of the incipient benzyl free radical in the transition states.

In terms of the concepts recently discussed by Hammond,[23] the transition state in the strongly exothermic reaction of chlorine atoms with the hydrocarbon will be very similar to reactants, whereas in the usually endothermic reaction of bromine atoms, the transition state will more closely resemble the products (benzyl radical and hydrogen bromide).

This interpretation appears to provide a reasonable explanation for the related phenomena observed in substitution reactions of isobutyric acid,[6,7] pentachloroethylbenzene[8] and alkyl halides.[6b,9,10]

One further peculiarity in the results remains to be considered. Resonance contributions in the transition state should not be important in the attack of chlorine atoms on the primary hydrogen atoms of cumene and *t*-butylbenzene. Consequently, we might expect that these hydrogen atoms should possess reactivities similar to those of typical alkanes. From observations of the reaction of free methyl radicals with cyclohexane[22] it would appear that the reactivity of the carbon–hydrogen bonds in this molecule is only slightly less than that of typical open-chain secondary hydrogen atoms. Therefore, it would be anticipated that in chlorination the reactivity of carbon–hydrogen bonds in cyclohexane would be somewhat smaller than the 3.2 value observed for the tertiary–primary reactivity ratio in 2,2,3-trimethylbutane.[15]

However, the ratio of attack by chlorine atoms of a cyclohexane hydrogen as compared to a primary hydrogen is 9.0 in cumene and 12.7 in *t*-butylbenzene.

There does not appear to be any factor which could significantly increase the reactivity of cyclohexane hydrogen over those for typical open-chain secondary hydrogen atoms. Consequently, the large ratio must be attributed to a decreased reactivity of the primary hydrogen atoms in cumene and *t*-butylbenzene toward chlorine atom attack.

It is now generally recognized that the phenyl group possesses a powerful electron-withdrawing inductive effect.[24,25] It is well established that electron-withdrawing substituents, such as chlorine, tend to reduce the activity of neighboring carbon-hydrogen bonds.[9] It appears reasonable, therefore, to ascribe the large ratios under discussion to the decreased reactivity of the primary hydrogen atoms in cumene and *t*-butylbenzene resulting from the inductive effect of the phenyl group.[26]

It appears, therefore, that in order to give a complete picture of the factors controlling the reactivity of carbon–hydrogen bonds in free radical reactions it is necessary to consider at least two major factors in addition to the bond dissociation energy: the extent of bond breaking in the transition state and the polar factors, both in the molecule under-

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(22) A. F. Trotman-Dickenson, *Quart. Revs.*, **7**, 198 (1953).

(23) G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

(24) The *p*Ka values of cyclohexanecarboxylic, acetic and phenylacetic acids are 4.88, 4.75 and 4.31, respectively; C. H. Spiers and J. F. Thorpe, *J. Chem. Soc.*, **127**, 538 (1925).

(25) B. M. Wepster, *Rev. trav. chim.*, **71**, 1159, 1171 (1952).

(26) It has been established recently that in the competitive halogenation of the side-chain of nuclear substituted toluenes, electron-withdrawing groups decrease, and electron-supplying groups increase, the activity of the carbon–hydrogen bonds; R. Van Helden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954); C. Walling and B. Miller Abstracts of Papers, 126th Meeting of the American Chemical Society New York, N. Y., Sept., 1954, p. 15R.

going attack and in the attacking atom or radical.[7b,27,28]

In conclusion, it is possible to account for the available data on relative reactivities in competitive attack on hydrogen atoms in terms of the transition state

$$\underset{\text{I}}{\mathrm{R{-}H\cdot X}} \longleftrightarrow \underset{\text{II}}{\mathrm{R^{+}\cdot H:X^{-}}} \longleftrightarrow \underset{\text{III}}{\mathrm{R\cdot H{-}X}}$$

The closer the actual transition state is to the products of the reaction (III), the more closely will the energy of activation follow the bond dissociation energy (or the resonance stabilization of the free radical, R·). When X· is highly electronegative, polar factors will become more significant. In other words, with X· highly electronegative, resonance structure II should be important and the activation energy should be affected greatly by substituents in R which affect the capacity of R to accommodate a positive charge. It should be recognized that the factors that determine this property do not necessarily parallel those which result in the stabilization of the free radical. Finally, in I we have the structure which would favor little contribution from resonance stabilization of R to the stability of the transition state.

Experimental Part

Materials.—Cyclohexane (C.P. grade) was passed through an activated silica gel column and rectified in a column packed with stainless steel helices that had been rated as having more than 50 theoretical plates. Fractions having a constant boiling point and refractive index were collected and stored over calcium hydride; b.p. 80.7°,[29] $n^{20}\mathrm{D}$ 1.4262. A cooling curve, measured by a calibrated copper–constantan thermocouple gave a freezing point of 6.50 ± 0.05°.

Toluene (Merck, C.P.) was rectified in the 50-plate column and constant boiling fractions were stored over calcium hydride; b.p. 110.6–110 7°, $n^{20}\mathrm{D}$ 1.4966. Cumene was purified similarly; b.p. 152.4–152.5°, $n^{20}\mathrm{D}$ 1.4915. Phillips 99 mole % minimum *t*-butylbenzene was passed through an activated silica gel column and rectified in the 50-plate column; b.p., 169.1–169.2°, $n^{20}\mathrm{D}$ 1.4925. Eastman Kodak Co. practical grade sulfuryl chloride was distilled through a Vigreux column and a freshly distilled, colorless middle fraction used for chlorination. Merck and Co., Inc., reagent grade bromine was used without purification. Chlorine was liquefied from a cylinder which had been bled to remove oxygen.

Halogenation Procedures.—The apparatus and procedure were similar to those previously described for photobromination,[5] sulfuryl chloride chlorination[15] and photochlorination.[15]

Analytical Procedures.—After the halogenation had been completed, the flask and its contents were weighed to determine whether any hydrocarbon vapors had been swept from the chlorination vessel by the stream of nitrogen used to introduce the halogen and by the hydrogen halide evolved. The loss was assigned to the two hydrocarbons being halogenated from their relative vapor pressures at the temperature of the exit condenser. The chlorination product then was refluxed under vacuum or degassed by a stream of prepurified nitrogen to remove all traces of hydrogen halide.

The total halogen content was determined on an aliquot by the Rauscher method.[30] Benzyl chloride was analyzed in the presence of chlorocyclohexane or neophyl chloride by reaction with a 1:1 piperidine–ethanol solution at room temperature as previously described.[20] It was found more convenient to determine benzyl bromide in the presence of bromocyclohexane by following the halide ion liberated by hydrolysis in 0.1 *N* alcoholic sodium hydroxide. At room temperature, the bromide ion concentration became constant within four to five hours for the concentrations of benzyl bromide employed. 2-Chloro-2-phenylpropane was analyzed in the presence of the primary isomer, chlorocyclohexane, neophyl chloride or benzyl chloride by hydrolysis in 80% ethanol at room temperature; the hydrochloric acid liberated was titrated with sodium hydroxide to the methyl red end-point. Hydrolysis usually was complete in two to three hours.

All procedures based on selective reactivity were checked thoroughly and standardized on prepared samples of the pure alkyl halides.

Calculation of Reactivity Ratios.—The products of a competitive chlorination are determined by the values of two rate constants

$$\mathrm{SH} + \mathrm{Cl}\cdot \xrightarrow{k_s} \mathrm{S}\cdot + \mathrm{HCl}$$

$$\mathrm{TH} + \mathrm{Cl}\cdot \xrightarrow{k_t} \mathrm{T}\cdot + \mathrm{HCl}$$

whose ratio

$$k_s/k_t = \log\,([\mathrm{SH}]_0/[\mathrm{SH}]_f)/\log\,([\mathrm{TH}]_0/[\mathrm{TH}]_f)$$

where brackets and subscripts are initial and final concentrations, represents the relative reactivity of the two hydrocarbons toward chlorine atoms. However, when the concentrations of the hydrocarbons vary for reasons other than reaction to form alkyl halides (*e.g.*, vaporization losses), the relative reactivity of the two hydrocarbons is calculated more satisfactorily by the expression

$$\frac{k_s}{k_t}\left(\frac{[\mathrm{SH}]}{[\mathrm{TH}]}\right)_{\mathrm{av}} = \frac{[\mathrm{SCl}]}{[\mathrm{TCl}]}$$

Because of losses of hydrocarbon through volatilization by the nitrogen stream and by the evolved hydrogen halide, the relative reactivities given in Table I were computed from the mean cyclohexane–toluene ratio rather than from the integrated expression.

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[27] Dr. E. C. Kooyman also has reached the conclusion that polar effects are highly important in free radical substitution reactions of the kind here discussed (private communication).

[28] The importance of polar effects in free radical copolymerization reactions has been generally recognized. See numerous papers in THIS JOURNAL by C. C. Price, F. R. Mayo, C. Walling, P. D. Bartlett and their co-workers.

[29] All boiling points were measured by a totally immersed N.B.S. calibrated thermometer and were corrected to 760 mm. by the dt/dp relationships given in the U. S. National Bureau of Standards Circular 461, "Selected Values of Properties of Hydrocarbons," Washington, D. C., 1947.

[30] W. H. Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **9**, 296 (1937).