

The arguments which have been presented on why the Hammett treatment should fail in reactions involving large resonance interactions with the substituents appear quite reasonable.⁸ It is possible that the correlations in Table IV appear better than they should because the data include relatively few *meta* substituents to permit an accurate determination of the true reaction constant.

On the other hand, data for numerous *meta* substituents are available for the ionization of triphenylcarbinyl chlorides in liquid sulfur dioxide (Fig. 11) and the frequency shifts in the infrared stretching frequency of the carbonyl group in sub-

stituted acetophenones (Fig. 12). Moreover, in these cases the reaction constants range from $\rho = -3.73$ to -12.30 . Nevertheless the correlation with the σ^+ -constants must be considered quite satisfactory.

The ability of these groups to correlate such diverse reactions suggests that there must be some fundamental property of substituent groups which is represented by the individual σ^+ -constants.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Solvent Effects in the Reactions of Free Radicals and Atoms. II. Effects of Solvents on the Position of Attack of Chlorine Atoms upon 2,3-Dimethylbutane, Isobutane and 2-Deuterio-2-methylpropane¹

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In the presence of a number of aliphatic solvents the photochlorination of 2,3-dimethylbutane produces 60% of 1-chloro-2,3-dimethylbutane and 40% of the 2-isomer. In the presence of certain aromatic solvents, and some non-aromatic materials, 2-chloro-2,3-dimethylbutane becomes the major reaction product. In 8 *M* benzene the 2-isomer is formed in 90% yield while in 12 *M* carbon disulfide the yield of 2-isomer is greater than 95% of the total yield of chloro-2,3-dimethylbutanes. This solvent effect, controlling the products of the reaction has been demonstrated to occur in the attack of the chlorine atom upon the hydrocarbon. It is concluded that chlorine atoms form a π -complex with the aromatic nucleus by an acid-base type interaction. These complexes are less reactive and therefore more selective than a free chlorine atom. The results indicate a method by which the reactivity and selectivity of free radicals and atoms can be altered and controlled. The importance of specific solvent effects in other free radical reactions is discussed.

It has been generally assumed that solvents have little effect upon the course and rate of free radical reactions.² This conclusion appears to be based mainly upon the effect of solvents, usually of varying polarity, upon the rate of homolytic dissociation, for example of hexaphenylethanes.³ The absence of solvent effects on the over-all rate of polymerization of styrene,⁴ and the copolymer structure observed in vinyl copolymerizations⁵ have been noted.⁶ However, it was felt that it would be

(1) Directive Effects in Aliphatic Substitution. XI. Presented before the Division of Organic Chemistry at the New York City Meeting of the American Chemical Society, September, 1957. A preliminary Communication appeared in *THIS JOURNAL*, **79**, 2977 (1957).

(2) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 237; C. Walling, "Free Radicals in Solutions," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 35.

(3) For a compilation of pertinent data, see W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, 1948, p. 47. Large solvent effects have been observed in the thermal decomposition of dibenzoyldiimide and benzoyl peroxide (J. E. Leffler and W. B. Boyd, *THIS JOURNAL*, **78**, 335 (1956)), but it is difficult to decide if these are true solvent effects or represent a change in the mechanism of decomposition or the actual intervention of the solvent in a chain decomposition. The rate of decomposition of phenylazotriphenylmethanes has been shown to be relatively independent of solvent, although large and compensating changes in entropy and enthalpy of activation have been noted as the solvent is varied (J. E. Leffler and R. A. Hubbard, *J. Org. Chem.*, **19**, 1089 (1954); M. G. Alder and J. E. Leffler, *THIS JOURNAL*, **76**, 1425 (1954)).

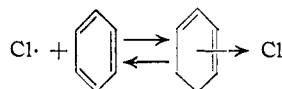
(4) R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 238 (1947).

(5) C. Walling and F. R. Mayo, *J. Polymer Sci.*, **3**, 898 (1948); F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and W. J. Wensch, *THIS JOURNAL*, **70**, 1527 (1948); C. C. Price and J. G. Walsh, *J. Polymer Sci.*, **6**, 239 (1951).

(6) Solvent effects in the free radical addition of hydrogen bromide to olefins have been discussed [F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940)] but conclusions are indefinite.

worthwhile to obtain data in other systems from which the magnitude of the solvent effect could be judged. The first free radical reaction that we examined was the photochlorination of a branched-chain hydrocarbon. Here, on the basis of admittedly scanty evidence, it had been suggested that the highly electrophilic chlorine atom should associate with the π -electrons of an aromatic solvent.⁷

All of the experimental evidence that we have obtained has been in agreement with this prediction. Aromatic solvents can dramatically alter the products of the photochemical chlorination of 2,3-dimethylbutane. Moreover, the magnitude of the solvent effect observed for various aromatic solvents suggests that the solvent effect arises from association of the chlorine atom with the π -electrons of the aromatic nucleus. This association produces a complexed chlorine atom (a π -complex) which has a lower reactivity and hence a greater selectivity than a free chlorine atom.



In the chlorination of 2,3-dimethylbutane in the absence of a solvent chlorine atoms attack a tert.-hydrogen atom about four times as readily as a prim.-hydrogen atom, presumably because of the greater resonance stabilization of a tert.-alkyl radical rela-

(7) G. A. Russell and H. C. Brown, *THIS JOURNAL*, **77**, 4031 (1955). This prediction has been discussed in more general terms by K. L. Nelson and H. C. Brown, "The Chemistry of Petroleum Hydrocarbons," B. T. Brooks, Editor, Reinhold Publishing Corp., New York, N. Y., 1955, Vol. III, p. 549.

TABLE I
SOLVENT EFFECTS IN THE PHOTOKLORINATION OF 2,3-DIMETHYLBUTANE

Solvent	Solvent concn. ^a	Rel. react. (tert./prim.) ^b		
		25°	40°	55°
Non-aromatic solvents				
2,3-Dimethylbutane	7.6	4.2	3.9	3.7
Carbon tetrachloride	4.0			3.5
Nitromethane	4.0			3.3
Methyl acetate	4.0			4.3
<i>n</i> -Butyric acid	4.0			4.1
Cyclohexane	4.0			3.6
Trichloroethylene	4.0			3.6
Propionitrile	4.0			4.0
Isobutyronitrile	4.0			4.0
Dimethylsulfolane	4.0			3.6
Silicon tetrachloride	4.0			3.7
Tetramethylsilane	4.4	4.2		
<i>n</i> -Pentane	4.8	4.3		
Cyclopentane	2.8		3.9	
<i>t</i> -Butyl alcohol	4.0			4.8
Dioxane	4.0			5.6
<i>n</i> -Butyl ether	4.0			7.2
N,N-Dimethylformamide	4.0			9.1
Thionyl chloride	4.0			7.3
Sulfur monochloride	4.0			14
Carbon disulfide	2.0	15		
Carbon disulfide	4.0	33		
Carbon disulfide	8.0	106		
Carbon disulfide	10.0	161		
Carbon disulfide	12.0	225		
Aromatic solvents				
Nitrobenzene	4.0			4.9
Benzoyl chloride	4.0			6.4
Trifluoromethylbenzene	4.0			6.9
Methyl benzoate	4.0			10.2
Chlorobenzene	2.0	9.0		
Chlorobenzene	4.0	17.1	13.5	10.2
Chlorobenzene	6.0	27.5		
Fluorobenzene	4.0			10.3
Thiophene	4.0			13.3
Benzene	2.0	11.0	8.6	8.0
Benzene	4.0	20	17.0	14.6
Benzene	8.0	49	40	32
Toluene	4.0			15.4
<i>o</i> -Xylene	4.0			15.0
Ethylbenzene	4.0			16.3
Phenyltrimethylsilane	4.0			16.4
Anisole	4.0			18.4
<i>p</i> -Xylene	4.0			18.6
Cumene	4.0			20.3
<i>m</i> -Xylene	4.0			22.4
<i>t</i> -Butylbenzene	1.0	9.3		
<i>t</i> -Butylbenzene	2.0	15		
<i>t</i> -Butylbenzene	4.0	35		24
Mesitylene	1.0			5.4
Mesitylene	4.0			25
Iodobenzene	4.0			31
Durene	1.0			5.8
Pentamethylbenzene	1.0			5.8
Hexamethylbenzene	1.0 ^c			6.7
Benzophenone	2.0			8.8
Diphenyl ether	2.0			10.3
Biphenyl	2.0			11.8
Phenyl sulfide	2.0			24

1-Chloronaphthalene	2.0	11
1-Chloronaphthalene	4.0	33
2- <i>t</i> -Butylnaphthalene	2.0	12
2- <i>t</i> -Butylnaphthalene	4.0	30
9- <i>n</i> -Butylantracene	2.0	5.0

^a At 25°, mole/liter. ^b Calculated from the equation, rel. react. (t./p.) = (2-chloro-2,3-dimethylbutane) 6/1-chloro-2,3-dimethylbutane. ^c Chloroform (1.2 *M*) used as a co-solvent.

tive to a prim.-alkyl radical.⁸ In the presence of certain aromatic solvents, and some non-aromatic solvents, the reactivity of the chlorine atom can be modified so that it attacks the tert.-hydrogen atom 50–300 times as readily as a prim.-hydrogen atom. The reactivity of a chlorine atom in these solvents is thus reminiscent of the selectivity observed in the attack of a bromine atom upon a branched-chain hydrocarbon.⁹

In the following paper the relative reactivities of a large number of carbon-hydrogen bonds in different molecules toward a chlorine atom in the presence of a limited number of solvents are discussed.¹⁰ All of these results are also in agreement with the assumption that the reactivity and selectivity of chlorine atoms can be altered in a predictable and controllable manner by the use of appropriate solvents. Future papers will consider the effects of solvents upon other free radical reactions.

Results

2,3-Dimethylbutane has been photochlorinated in the presence of a large number of solvents. In some cases the solvent itself was attacked by chlorine atoms while in other cases the solvent was inert. Chlorinations were performed by the addition of a small amount of gaseous chlorine (approximately 0.005 mole) to an excess of the hydrocarbon (0.30–0.10 mole). Thus, the mole % chlorination was in the range of 1–5% and polychlorination was not a complicating factor. The products of the photochlorination of 2,3-dimethylbutane were analyzed by gas-liquid chromatography (GLC). The only alkyl chlorides found were 1- and 2-chloro-2,3-dimethylbutane.

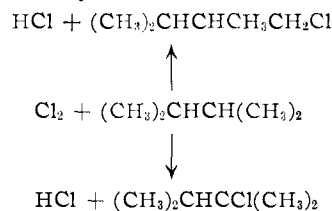


Table I summarizes the results of photochlorinations wherein the structure of the solvent, the concentration of the solvent and the temperature have been varied.

The data of Table I indicate that solvents can indeed profoundly influence the products of the chlorination of 2,3-dimethylbutane. Many aliphatic solvents have but a slight effect upon the products of the chlorination, whereas aromatic solvents have a pronounced effect upon the products of the reac-

(8) This point is discussed in detail in ref. 10.

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

(10) G. A. Russell, *ibid.*, **80**, 4997 (1958).

tion. This solvent effect increases with the concentration of the aromatic hydrocarbon and is more pronounced at the lower temperatures.

Some of the solvents listed in Table I were themselves quite reactive toward chlorine atoms. For chlorinations performed in the presence of cyclohexene, trichloroethylene and 9-*n*-butylanthracene, the major reaction products were the products of addition of chlorine to the solvent. Dioxane and *n*-butyl ether yielded mainly the products of chlorine substitution in the solvent. Quantitative data on the competition for a chlorine atom between 2,3-dimethylbutane and hydrocarbons such as *n*-pentane, cyclopentane, tetramethylsilane and toluene are given elsewhere.¹⁰ The yields of alkyl chlorides were low for chlorinations performed in the presence of iodobenzene and phenyl sulfide, presumably because of the concurrent formation of the dichloride addition products. Chlorinations in the presence of carbon disulfide did not appear to yield appreciable chlorination products of the solvent since only minor amounts of carbon tetrachloride were detected by GLC.

In the experiments summarized in Table I the concentration of 2,3-dimethylbutane varied considerably and it was therefore necessary to demonstrate the effect of this variable upon the products of the reaction. Table II demonstrates that the solvent effects observed for aromatic solvent or carbon disulfide are independent of the concentration of 2,3-dimethylbutane.

TABLE II

EFFECT OF THE CONCENTRATION OF 2,3-DIMETHYLBUTANE UPON THE CHLORINATION PRODUCTS

2,3-Di- methyl- butane concn., moles/liter	Diluent	Temp., °C.	Rel. react. (t./p.)
	In benzene (4.0 <i>M</i>)		
1.4	Carbon tetrachloride	25	24
3.0	Carbon tetrachloride	25	21.5
4.9	None	25	20
1.6	<i>n</i> -Pentane	25	20
4.9	None	40	17.5
2.3	Cyclopentane	40	16.5
	In <i>t</i> -butylbenzene (4.0 <i>M</i>)		
2.8	None	25	35
1.1	<i>n</i> -Pentane	25	37
1.2	Tetramethylsilane	25	33
2.8	None	40	32
1.0	Cyclopentane	40	29
	In carbon disulfide (12.0 <i>M</i>)		
2.1	None	25	250
1.1	<i>n</i> -Pentane	25	253
0.80	Tetramethylsilane	25	231
2.1	None	40	220
1.1	Cyclopentane	40	220

The question of whether or not the products of the chlorination of 2,3-dimethylbutane are a true measure of the point of attack of a chlorine atom upon the hydrocarbon was considered since processes are imaginable wherein aromatic solvents preferentially react with one of the alkyl radicals. Table III demonstrates that for several of the sys-

tems studied hydrogen chloride and organic chlorides were formed in a 1:1 mole ratio. The formation of organic chloride and hydrogen chloride in a 1:1 mole ratio can occur only in the absence of additive chlorination of the aromatic ring. Furthermore, it can occur only when each alkyl radical formed eventually gives rise to a molecule of alkyl chloride. Thus, aromatic solvents cannot influence the chlorination products of 2,3-dimethylbutane by preferentially scavenging one of the intermediate radicals. Chlorinations performed in the presence of benzene also were examined for the formation of chlorobenzene. No chlorobenzene could be detected by GLC from a photochlorination of 2,3-dimethylbutane in the presence of 8 *M* benzene. Since 0.0001 mole of chlorobenzene could have been detected, less than 4% of the 0.005 mole of chlorine used entered into aromatic substitution.

TABLE III

CHLORINE BALANCE FOR THE PHOTOCHEMICAL CHLORINATION OF 2,3-DIMETHYLBUTANE IN THE PRESENCE OF AROMATIC SOLVENTS

Solvent	Solvent concn., moles/liter	Temp., °C.	Organic chloride, mole × 10 ⁻³	Hydrogen chloride, mole × 10 ⁻³
Benzene	2	40	5.2	5.1
Benzene	8	40	5.5	5.5
Benzene	4	25	5.1	5.1
Benzene	4	55	4.5	4.7
<i>t</i> -Butylbenzene	4	40	5.2	5.1

Conclusive evidence that the solvent effect in these photochlorinations occurs in the attack of a chlorine atom upon the hydrocarbon was obtained from a study of the chlorination of isobutane and its 2-deuterio derivative. In Table IV are summarized the results of these experiments.

TABLE IV

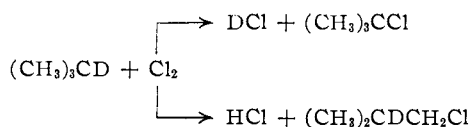
PHOTOCHEMICAL CHLORINATION OF ISOBUTANE AND 2-DEUTERIO-2-METHYLPROPANE AT -15°

Hydrocarbon	Solvent	t.-BuCl/ <i>i</i> -BuCl	DCl/HCl
Isobutane	Isobutane	4.5:9.0	
Isobutane	5.9 <i>M</i> chlorobenzene	29:9.0	
2-Deuterio-2-methylpropane	Isobutane	3.5:9.0 ^a	2.9:9.0 ^a
2-Deuterio-2-methylpropane	5.9 <i>M</i> chlorobenzene	18:9.0 ^a	14:9.0 ^a

^a Corrected for the presence of 5% isobutane.

Table IV demonstrates that chlorobenzene has a pronounced solvent effect in the photochlorination of isobutane at -15°. In the absence of added solvent the tert.-hydrogen atom is 4.5 times as reactive as the prim.-hydrogen atom, as judged from the products of the reaction (analysis by GLC). In the presence of an equal volume of chlorobenzene the tert.-hydrogen atom in isobutane is 29 times as reactive as a prim.-hydrogen atom. The photochlorination of 2-deuterio-2-methylpropane in the absence of added solvent produced deuterium and hydrogen chlorides in the ratio 2.9 to 9 while

tert.-butyl and isobutyl chlorides were formed in the ratio 3.5 to 9.



These ratios are felt to be essentially within experimental error. The deuterium-isotope effect for the attack of a chlorine atom upon a tert.-hydrogen or deuterium atom of isobutane is calculated to be in the range 1.3–1.5. In the presence of an equal volume of chlorobenzene deuterium and hydrogen chlorides were formed in the ratio 14:9 while tert.-butyl and isobutyl chlorides were formed in the ratio 18:9. The deuterium isotope effect in the presence of chlorobenzene is in the range 1.6–2.1, and the results indicate that not more than 15% of the isobutyl radicals formed may have given rise to tert.-butyl chloride, either by rearrangement or reaction with the parent hydrocarbon. The deuterium and hydrogen chloride ratios of Table IV indicate that the attack of a chlorine atom upon 2-deuterio-2-methylpropane is 4.9 times more selective in the presence of 5.9 *M* chlorobenzene, while from the *t*-butyl and isobutyl chloride ratios it appears that the chlorine atom is 5.1 times as selective in the presence of 5.9 *M* chlorobenzene. The alkyl chlorides formed in the presence of aromatic solvents are thus a good measure of the point of attack of chlorine atoms upon the hydrocarbon. Previously we had reached a similar conclusion in regard to the products of photochlorination in the absence of aromatic solvents.¹¹

Discussion

Aromatic Solvents.—In the preceding section we have demonstrated that solvents, particularly aromatic solvents, can drastically alter the point of attack of chlorine atoms upon a branched-chain hydrocarbon. This does not appear to be a general solvent effect since a variety of solvents of varying polarity, including carbon tetrachloride, nitromethane, methyl acetate, *n*-butyric acid, propionitrile, dimethylsulfolane, silicon tetrachloride and tetramethylsilane, had a negligible effect upon the products of the reaction.

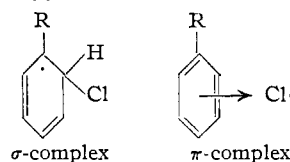
The solvent effect is small for aromatics containing an electron-withdrawing substituent (nitrobenzene, benzoyl chloride, trifluoromethylbenzene) and large for aromatics with electron-supplying substituents (*t*-butylbenzene, mesitylene, hexamethylbenzene). The rather specific action of aromatic solvents suggests that the solvent effect results from the formation of a complex between the chlorine atom and the aromatic nucleus.¹² By complex formation the reactivity of the chlorine atom would be decreased and its selectivity in attack upon a system of carbon–hydrogen bonds in-

(11) H. C. Brown and G. A. Russell, *THIS JOURNAL*, **74**, 3995 (1952).

(12) The possibility that in aromatic solvents aliphatic hydrocarbons can be chlorinated by a process that does not involve a free radical reaction was considered. No chlorination of 2,3-dimethylbutane in the presence of benzene but absence of light at 55° could be detected. Furthermore, a solution of 2,3-dimethylbutane in benzene in the presence of 1 wt. % of ferric chloride gave only chlorobenzene and none of the chloro-2,3-dimethylbutanes.

creased. The solvent effect of a given aromatic solvent would thus increase with the stability of the complex.¹³

Two possible complexes, a σ -complex and a π -complex,^{7,14} suggest themselves.



Of these two possible intermediates the σ -complex appears unlikely. The observation that addition or substitution reactions between chlorine and benzene are unimportant when 2,3-dimethylbutane is chlorinated in that solvent can be taken as evidence against a σ -complex intermediate. The relative stabilities of these σ -complexes should be determined mainly by resonance stabilization. If this is the case some correlation between the observed solvent effects and the relative rates of phenylation of these aromatic materials would be expected. However, there is no obvious correlation. In Fig. 1 the relative reactivities of various aromatic materials toward phenyl radicals, as cited by Augood and Williams,¹⁵ have been plotted as a function of the solvent effect observed when these materials are used as solvents in the chlorination of 2,3-dimethylbutane. Nor is any correlation found if the methyl-affinities of these substances are considered.¹⁶

The observed solvent effects are those expected if a π -complex were involved. The stability of the π -complex should increase with an increase in the basicity or electron density of the aromatic ring.¹⁷ In fact, there is apparently a quantitative relationship between the magnitude of the solvent effect and basicity of the solvent. Figure 2 demonstrates this relationship wherein relative values of the log of the observed relative reactivities in the presence of 4 *M* solvent at 55° has been plotted as a function of the log of the relative basicity of the aromatic solvent as measured by the equilibrium constant for interaction with hydrogen chloride at –78.5°. The linear free energy relationship between these two measurements strongly suggests that both measurements involve the same phenomenon. Even thiophene has a solvent effect proportional to its basicity.

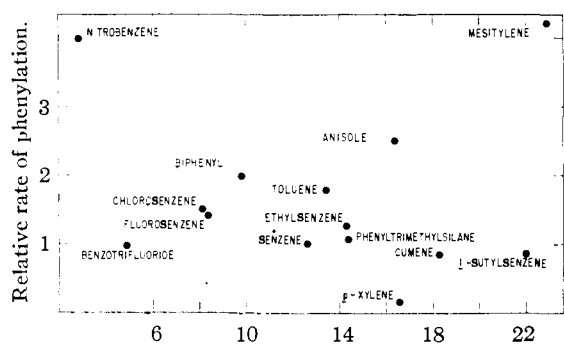
(13) The possibility exists that a complex might be so stable that the complexed chlorine atom would be unable to abstract a hydrogen atom from the hydrocarbon. In this case, only the chlorine atom in equilibrium with the complex could attack the hydrocarbon and, although the rate of the chlorination should be greatly depressed, the products of the chlorination would not be affected. We believe we have detected a somewhat similar situation when olefinic substances or anthracene derivatives are used as solvents. These results are discussed in the section on non-aromatic solvents.

(14) H. C. Brown and J. D. Brady, *THIS JOURNAL*, **74**, 3570 (1952).

(15) D. R. Augood and G. H. Williams, *Chem. Revs.*, **57**, 123 (1957).

(16) W. J. Heilman, A. Rembaum and M. Szwarc, *J. Chem. Soc.*, 1127 (1957).

(17) Chlorine molecules also form π -complexes with an aromatic nucleus [H. Murakami, *J. Chem. Phys.*, **23**, 1957 (1955)] and the stabilities of these complexes should vary in the same manner as the stability of the π -complex of a chlorine atom. Interactions between molecular chlorine and aromatic rings are of no concern in the present discussion since we have demonstrated that the solvent effect occurs in the attack of a chlorine atom upon the hydrocarbon.



Relative reactivity (tert./prim.) of hydrogen atoms of 2,3-dimethylbutane.

Fig. 1.—Relative rates of phenylation of aromatic materials at 80° as a function of the effect of these substances (4.0 M) on the photochlorination of 2,3-dimethylbutane. Corrections for side-chain attack in phenylation have been made.

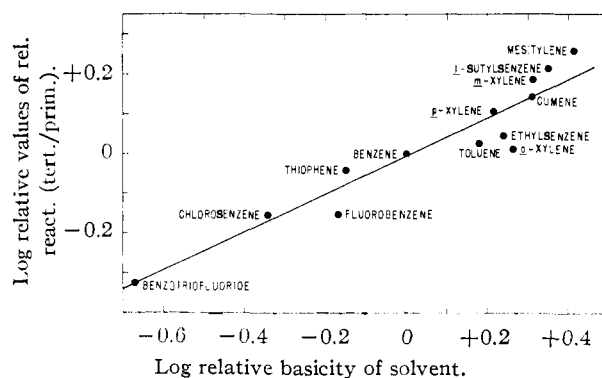


Fig. 2.—Linear free energy relationship between the basicity of the solvent and the relative reactivity of the hydrogen atoms of 2,3-dimethylbutane at 55°.

The relative stabilities of numerous other π -complexes of aromatic rings, particularly those involving the interactions with silver ion and molecular iodine, are known.¹⁸ The stabilities of these π -complexes are qualitatively in agreement with the solvent effects reported in Table I. Thus, toward silver ion π -complex stability increases in the order $C_6H_6 < p$ -xylene $<$ naphthalene $<$ biphenyl¹⁹; whereas in the photochlorination of 2,3-dimethylbutane, solvents affect the position of attack of a chlorine atom in the manner, benzene $<$ p -xylene $<$ 1-chloronaphthalene $<$ biphenyl $<$ t -butylnaphthalene. The relative stability of complexes between aromatics and molecular iodine shows the order of stability, benzene $<$ p -xylene $<$ durene $<$ mesitylene $<$ pentamethylbenzene $<$ hexamethylbenzene.^{18, 20} As solvents in chlorination the following relative effectiveness is indicated, benzene $<$ p -xylene $<$ mesitylene $<$ durene $<$ pentamethylbenzene $<$ hexamethylbenzene.

Another measure of the electron density of an aromatic ring correlates the solvent effects of many of the negatively substituted benzene deriva-

(18) For a summary, see L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

(19) L. J. Andrews and R. M. Keefer, *THIS JOURNAL*, **71**, 3644 (1949).

(20) R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955).

tives in Table I. Using the Hammett σ_{meta} -constant²¹ as a measure of basicity of the aromatic ring the linear relationship of Fig. 3 is obtained. In Fig. 3, σ_{meta} for the substituent of the solvent has been plotted as a function of the log (rel. react. (t./p.)-3.7). The reason for the use of the

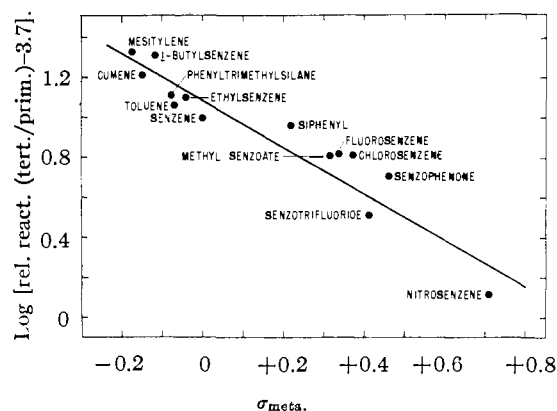
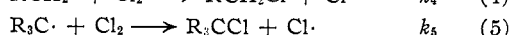
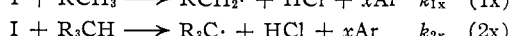
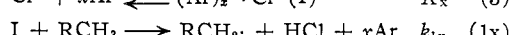
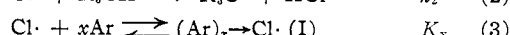
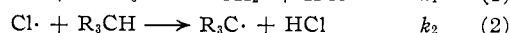
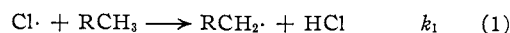


Fig. 3.—Correlation between rel. react. and σ_{meta} for aromatic solvents at 55°.

function, rel. react. (t./p.)-3.7, will be discussed in the next section. The constants used are those given by Jaffé²¹ except for the trimethylsilyl group where the value given by Roberts has been used.²² σ_{meta} -Constants are not listed for isopropyl and phenacyl groups and σ_{para} was used instead. A plot very similar to that of Fig. 3 is obtained if σ_{para} is used exclusively. Biphenyl and benzophenone are included in Fig. 3 along with mononuclear aromatic hydrocarbons. A statistical correction has been applied to the data in that the solvent effect of substances with two aromatic rings at a 2 M concentration has been compared with the solvent effect observed for mononuclear materials at a 4 M concentration.

The correlations of Figs. 2 and 3 establish the effect of aromatic solvents in a photochlorination reaction as one related to π -complex formation. In the presence of an aromatic solvent the chain propagation reactions should therefore be formulated



The effect of aromatic solvents is to give rise to an appreciable concentration of I which attacks a hydrocarbon with a selectivity (k_{2x}/k_{1x}) much greater than that observed for an uncomplexed chlorine atom (k_2/k_1).

(21) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184; H. H. Jaffé, *Chem. Revs.*, **54**, 191 (1954).

(22) J. D. Roberts and C. M. Regan, *THIS JOURNAL*, **75**, 4102 (1953).

Further evidence that I is less reactive²³ and therefore more selective than a free chlorine atom is provided by the magnitude of the deuterium-isotope effect in the photochlorination of isobutane and 2-deuterio-2-methylpropane. In the absence of aromatic solvents at -15° the isotope effect is small, in the range 1.2–1.5. In the presence of 5.9 *M* chlorobenzene the isotope effect is larger, 1.5–2.1, indicating a greater degree of bond-breaking in the attack of I upon a carbon–hydrogen bond than for the attack of a free chlorine atom upon a carbon–hydrogen bond.

Influence of Temperature and Solvent Concentration.—The effect of temperature on the products of the liquid phase photochlorination of branched-chain hydrocarbons, in the absence of a complexing solvent, is slight.⁵ The present data indicate that the *t*-hydrogen atom of 2,3-dimethylbutane is 4.2 times as reactive toward a chlorine atom as is a *p*-hydrogen atom at 25° . At 40 and 55° the relative reactivities are 3.9 and 3.7, respectively. These data indicate a difference in energy of activation for attack of a chlorine atom upon *p*- and *t*-hydrogen atoms, $E_a(p.) - E_a(t.)$, of 0.7 kcal. mole⁻¹. In the presence of aromatic solvents a larger temperature effect is observed. For example, in the presence of 4 *M* benzene an apparent energy of activation, $E_a(p.) - E_a(t.)$, of 2.1 kcal. mole⁻¹ is indicated. In 8 *M* benzene the apparent energy of activation difference is still higher, 2.7 kcal. mole⁻¹. Because of the number of chain-propagating steps (eq. 1–5), and the existence of possible equilibria, an exact interpretation of this difference in energy of activation is difficult.

The effect of the concentration of aromatic hydrocarbon on relative reactivity is demonstrated in Fig. 4. The solvent effect becomes increasingly important as the concentration of aromatic hydrocarbon increases. The curves in Fig. 4 empirically fit the relationship

$$\text{rel. react.} = k + k'[\text{Ar}] + k''[\text{Ar}]^2 \quad (\text{A})$$

Equation A can be consistent with eq. 1–5 if certain requirements are met. The requirements are that there are two π -complexes, $x = 1$ and $x = 2$, and that $k_{11}K_1[\text{Ar}]$ and $k_{12}K_2[\text{Ar}]^2$ are small compared with k_1 .²⁴ Under these conditions B can be derived.

$$\text{rel. react. (t./p.)} = \frac{(k_2 + k_{21}K_1[\text{Ar}] + k_{22}K_2[\text{Ar}]^2)6}{k_1} \quad (\text{B})$$

We have valuated $k_{21}K_1/k_1$ and $k_{22}K_2/k_1$ from the data given in Table I. The values listed in Table V were obtained as the best constants, determined

(23) This interpretation predicts that aromatic solvents should decrease the rate of attack of a chlorine atom upon a hydrocarbon. Qualitatively, chlorine reacts extremely readily with 2,3-dimethylbutane in the presence or absence of aromatic solvents. In any event, the effect of solvents on the over-all rate of reaction of chlorine is not necessarily a true measure of the effect of solvents on the rate of reaction of chlorine atoms since solvents may affect other steps in this chain reaction. It is of considerable interest that F. R. Mayo and W. B. Hardy [THIS JOURNAL, **74**, 911 (1952)] found that naphthalene retards the rate of photobromination of toluene. It is not certain whether this is a true solvent effect or an inhibition effect resulting from the scavenging of bromine atoms.

(24) The constants k_{11} , k_{12} , k_{21} , k_{22} , K_1 and K_2 refer to reactions 1x and 2x and 3 with *x* equal to 1 and 2, respectively.

by the method of least squares, correlating this data with the quadratic equation A. In column 5 of Table V are given the root mean squares of the deviations between experimental and calculated relative reactivities.

TABLE V
EFFECT OF SOLVENT CONCENTRATION ON RELATIVE REACTIVITY

Solvent (temp., °C.)	k_2/k_1	$k_{21}K_1/k_1$	$k_{22}K_2/k_1$	Standard deviation
Benzene (25)	0.717	0.397	0.0665	0.21
Benzene (40)	.633	.325	.0546	.23
Benzene (55)	.600	.310	.0351	.18
Chlorobenzene (25)	.691	.300	.0583	.11
<i>t</i> -Butylbenzene (25)	.733	.558	.178	.32

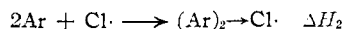
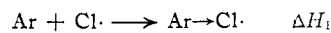
The values of $k_{21}K_1/k_1$ are all larger than the values of $k_{22}K_2/k_1$. This is quite reasonable since not only would $k_{21} > k_{22}$ but $K_1 > K_2$. Both $k_{21}K_1/k_1$ and $k_{22}K_2/k_1$ increase as the solvent is changed from chlorobenzene to benzene to *t*-butylbenzene. This effect may indicate that K_1 and K_2 are more dependent upon the nature of the aromatic hydrocarbon than are k_{21} and k_{22} . It is expected that k_{21} and k_{22} would decrease as the solvent is changed from chlorobenzene to benzene to *t*-butylbenzene.²⁵ The relative values of K_1K_2/k_1 for chlorobenzene, benzene and *t*-butylbenzene are in excellent agreement with the relative basicities of these materials as a linear free energy plot.¹⁴ The values of $k_{22}K_2/k_1$ do not give a good quantitative agreement, suggesting relationships similar to that given in Fig. 2 are more likely to occur at low concentrations of the aromatic diluent.

We are now in a position to return to the discussion of the effect of temperature upon photochlorinations in aromatic solvents. From the data of Table V, it is possible to obtain values of $E_a(21) + \Delta H_1 - E_a(1)$ and $E_a(22) + \Delta H_2 - E_a(1)$ for chlorinations of 2,3-dimethylbutane in benzene solution.

$$E_a(21) + \Delta H_1 - E_a(1) = -1.2 \text{ kcal. mole}^{-1}$$

$$E_a(22) + \Delta H_2 - E_a(1) = -4.6 \text{ kcal. mole}^{-1}$$

Since $E_a(21)$ and $E_a(22)$ should be higher than $E_a(1)$, minimum values of ΔH_1 and ΔH_2 can be estimated. In benzene ΔH_1 is not less than -1.2 kcal. mole⁻¹ and ΔH_2 is not less than -4.6 kcal. mole⁻¹.



Thus, the interaction of a chlorine atom with a benzene molecule to form a 1:1 π -complex is exo-

(25) We have not pursued this approach further because of the inherent possibilities of error. Equation A, although the simplest equation that fits our data, is not necessarily the correct kinetic equation. The correct equation may involve more than three parameters or may require a statistical treatment. Furthermore the equilibrium constants involved may themselves vary with the composition of the medium. In view of these possible complication factors the consistency of the data of Table V is gratifying. For the five solvents listed in Table V the data were also fitted by cubic equations (rel. react. = $a + b[\text{Ar}] + c[\text{Ar}]^2 + d[\text{Ar}]^3$) determined by the method of least squares. In only one case (benzene, 25°) were all coefficients of the cubic equation positive. In other cases, *c* (*t*-butylbenzene) or *d* (chlorobenzene; benzene, 40 and 55°) was negative and the equation had no significance.

thermic by at least 1.2 kcal. mole⁻¹ in the temperature range 25–55°. Since it seems likely that $2\Delta H_1 > \Delta H_2$, probably $-\Delta H_1 > 2.3$ kcal. mole⁻¹.

If the interpretation given previously is correct, it follows that in an aromatic solvent chlorine atoms are mostly complexed. For example, in the photochlorination of 2,3-dimethylbutane in the presence of 8 M benzene at 25°, 1- and 2-chloro-2,3-dimethylbutane are formed in the ratio of 1 to 8. The kinetic treatment has indicated that most likely only the free chlorine atom can attack primary hydrogen atoms. Furthermore, the free chlorine atom attacks the p- and t.-hydrogen atoms of 2,3-dimethylbutane at the relative rates of 1 to 4.2 at 25°. Therefore, attack by free chlorine atoms, in the presence of 8 M benzene, should have produced 0.7 part of 2-chloro-2,3-dimethylbutane for each part of 1-chloro-2,3-butane while attack by complexed chlorine atom produced 7.3 parts of 2-chloro-2,3-dimethylbutane. If free and complexed chlorine atoms attack the t.-hydrogen atom of 2,3-dimethylbutane with equal ease ($k_2 = k_{21} = k_{22}$), it follows that free and complexed chlorine atoms are present in the ratio of 1:10.4. Thus, at least 91% of the chlorine atoms are complexed in the presence of 8 M benzene. Actually, it is believed that $k_2 \gg k_{21}$ or k_{22} and that $\gg 91\%$ of the chlorine atoms are complexed with the aromatic nucleus in the presence of 8 M benzene.

In the previous section it was demonstrated that the relationship C exists.

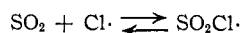
$$\log [\text{rel. react. (t./p.)} - 3.7] = \rho\sigma \quad (\text{C})$$

From B and C with 6 $k_2/k_1 = 3.7$ and $[\text{Ar}] = 4$ M, equation D can be derived.

$$\log (k_{21}K_1 + 4k_{22}K_2) + \log (24/k_1) = \rho\sigma$$

From Fig. 3 it is obvious that $\log (k_{21}K_1 + k_{22}K_2)$ decreases rather smoothly with an increase in σ_{meta} (a decrease in basicity) of the solvent substituent. Again, k_{21} and k_{22} are expected to increase with a decrease in the basicity of the solvent whereas K_1 and K_2 should decrease. Thus the equilibrium constant K appears to be more important in determining the relative reactivities in a given solvent than the rate constants k_{2x} .

Non-aromatic Solvents.—As demonstrated in Table I, many non-aromatic solvents have little effect upon the products of the photochlorination of 2,3-dimethylbutane. However, solvent effects were noticed for *t*-butyl alcohol, dioxane, *n*-butyl ether, dimethylformamide, thionyl chloride, sulfur monochloride, carbon disulfide and for various alkyl iodides (not listed in Table I). In certain of these solvents chlorine atoms may react with the solvent to form a new radical involving an electron-pair bond, similar to the interaction between sulfur dioxide and chlorine atoms.^{7,27} Other solvent ef-



fects observed for non-aromatic solvents cannot be interpreted easily in terms of such intermediates. *t*-Butyl alcohol, dioxane and *n*-butyl ether all displayed solvent effects and it appears possible that

(26) The formation of a π -complex between iodine and benzene is exothermic to the extent of 1.2–3.4 kcal. mole⁻¹ over this temperature range (ref. 20).

(27) G. A. Russell, *THIS JOURNAL*, **80**, 5002 (1958).

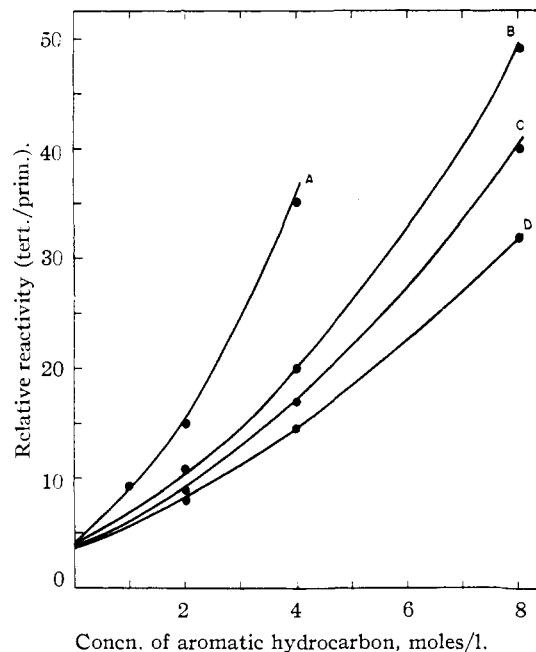
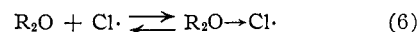


Fig. 4.—Effect of the concentration of aromatic hydrocarbons on the rel. react. of the hydrogen atoms of 2,3-dimethylbutane; A, *t*-butylbenzene, 25°; B, benzene, 25°; C, benzene, 40°; D, benzene, 55°.

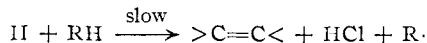
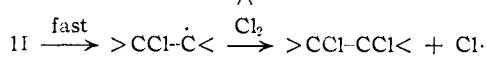
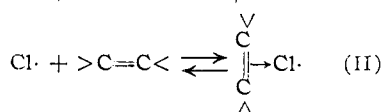
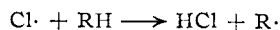
these materials can undergo acid-base interactions with chlorine atoms similar to the π -complex formation observed in aromatic solvents.



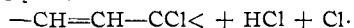
If equilibrium 6 occurs with oxygenated compounds an analogous reaction should occur even more readily with sulfur and iodine atoms which have a higher polarizability. The solvent effects of diphenyl ether, diphenyl sulfide and iodobenzene upon the chlorination of 2,3-dimethylbutane were therefore studied. Diphenyl sulfide proved to be more effective than diphenyl ether in increasing the selectivity of a chlorine atom. For a given molar concentration diphenyl sulfide was one of the most effective solvents found. This, of course, must be partially due to the fact that there are two phenyl groups per molecule. Iodobenzene also proved to be an extremely efficient solvent, even more so than mesitylene, and its effectiveness as a solvent was completely out of line with its basicity. When iodobenzene was used as a solvent the formation of iodobenzene dichloride was a competing reaction and the possibility exists that the solvent effects of both diphenyl sulfide and iodobenzene are largely due to the formation of intermediate radicals involving expansion of the valence shell of sulfur and iodine. Experimental difficulties were encountered in a study of solvent effects of alkyl iodides and sulfides. In the presence of diethyl sulfide, 2,3-dimethylbutane was not photochlorinated. We presume the chlorine was consumed by the sulfide to yield the dichloride or its decomposition product. When 4.0 M ethyl iodide was used as a solvent in the photochlorination of 2,3-dimethylbutane at 55° iodine was liberated in the chlorination, the addition of 0.005 mole of chlorine

producing 0.0016 mole of iodine. Analysis by GLC indicated the presence of ethyl chloride and an appreciable amount of 2-chloro-2,3-dimethylbutane but no 1-chloro-2,3-dimethylbutane. From this data we calculate an apparent relative reactivity (t./p.) of > 600 to 1. Repetition of the experiment in the absence of illumination produced large amounts of iodine or iodine monochloride, but neither of the chloro-2,3-dimethylbutanes could be detected. Use of 4.0 *M* *n*-butyl iodide as a solvent at 55° also gave large amounts of iodine, *n*-butyl chloride and 2-chloro-2,3-dimethylbutane. The 1-chloro-2,3-dimethylbutane could be detected in this instance and the apparent relative reactivity (t./p.) was 390 to 1. Finally, the photochlorination of 2,3-dimethylbutane in the presence of 0.03 *M* iodine (0.00076 mole) was performed. The reaction was inhibited since chlorine was lost from the system (see Experimental section), but an appreciable amount of 2-chloro-2,3-dimethylbutane and some 1-chloro-2,3-dimethylbutane were found by GLC. The apparent relative reactivity (t./p.) was 141 to 1. Again either a charge-transfer complex or a complex with an expanded valence shell can be imagined as an intermediate.²⁸

Neither cyclohexene nor trichloroethylene affected the relative yields of 1- and 2-chloro-2,3-dimethylbutanes. Moreover, in the presence of these solvents only small amounts (roughly 10% of the theoretical amount) of the chloro-2,3 dimethylbutanes were formed. Olefinic materials readily form π -complexes with silver ion²⁹ or hydrogen chloride¹⁴ and it was expected that a similar complex would be formed with the chlorine atom. A possible explanation is connected with the fact that only a small amount of aliphatic substitution occurred.



As pictured, the π -complex II decomposes to the σ -complex which rapidly yields the chlorine addition product, or in certain cases the allylic chloride, $-\text{CH}_2-\text{CH}-\text{CCl}< + \text{Cl}_2 \longrightarrow$



in preference to abstracting a hydrogen atom from 2,3-dimethylbutane (RH).

(28) Molecular chlorine itself may be able to complex the chlorine atom and thereby alter its selectivity. Evidence for this effect appears to be available. When isobutane is chlorinated in the liquid phase under conditions wherein the concentration of chlorine is extremely low at all times, the tert.-hydrogen atom is 4.2-4.5 times as reactive as the prim.-hydrogen atom at -15° (ref. 7). However, when isobutane and a large volume of chlorine, again in the liquid phase, are mixed in a sealed tube and illuminated at -15° careful analysis of the reaction products has indicated that the tert.-hydrogen atom is 7.5 times as reactive as a prim.-hydrogen atom [H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935); **28**, 333 (1936)]. Up to this time no explanation for this discrepancy has been advanced (see footnote 7, ref. 7).

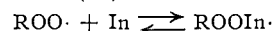
(29) S. Winstein and H. J. Lucas, *THIS JOURNAL*, **60**, 836 (1938).

The above proposal was tested in the following manner. Anthracene is a very basic hydrocarbon³⁰ possessing nearly olefinic reactivity at the 9,10-positions. It was predicted therefore that anthracene and its derivatives should have a very small solvent effect. Anthracene itself proved too insoluble to be used in our studies, but the lower-melting 9-*n*-butylanthracene was satisfactory. In the presence of 2 *M* 9-*n*-butylanthracene over 99% of the chlorine added to the aromatic nucleus. However, small amounts of the chlorodimethylbutanes were formed. The relative reactivity (t./p.) was found to be 5.0 at 55° . In the presence of the less basic 2-chloronaphthalene (2 *M*) a rel. react. (t./p.) of 11 to 1 was observed. These results confirm our supposition that olefinic materials do not display a solvent effect in the photochlorination of 2,3-dimethylbutane because the π -complexes, although formed readily, nearly always collapse to the σ -complex before abstracting a hydrogen atom.

Solvent Effects in Other Free Radical Reactions.

—The present paper has described a rather specific type of solvent effect observed in the photochlorination of 2,3-dimethylbutane. The following paper will provide numerous other examples of this type of solvent effect in photochlorination reactions. It appears appropriate to wonder whether solvent effects of this magnitude can be found in other free radical reactions.

Solvent effects in photochlorinations have been interpreted as arising from an acid-base type of interaction between a chlorine atom and a basic solvent. A chlorine atom is an extremely electrophilic particle as evidenced by a pronounced polar effect in many of its reactions.³¹ In the vapor phase it has an electron affinity of 88.2 kcal. mole⁻¹.³² The electron affinities for other common radicals are fluorine, 83.5; bromine, 81.6; iodine, 74.6; HOO·, 70; hydroxyl, 50; triphenylmethyl, 48; phenoxy, 27; methyl, 25.³² The specific solvent effects discussed in this paper should decrease with a decrease in the electron affinity of the atom or radical. Thus, these solvent effects should be most pronounced for the reaction of halogen atoms and other highly electrophilic atoms or radicals, such as peroxy or alkoxy radicals. In this connection, it is of interest that Hammond and Boozer have suggested that the inhibition of autoxidation by phenols or aniline derivatives involves the formation of complexes between peroxy radicals and inhibitor molecules (In).³³



There are little data available concerning the absolute rate constants of propagation and termination reactions in autoxidations performed in solution.

(30) See for example W. L. Petrolas, *J. Chem. Phys.*, **26**, 429 (1957).

(31) A. B. Ash and H. C. Brown, *Record Chem. Progr.*, **9**, 81 (1948); C. C. Price and H. Morita, *THIS JOURNAL*, **75**, 3683 (1953); R. Van Helden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954); H. C. Brown and A. B. Ash, *THIS JOURNAL*, **77**, 4019 (1955); G. A. Russell and H. C. Brown, *ibid.*, **77**, 4578 (1955); C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957).

(32) H. O. Prichard, *Chem. Revs.*, **52**, 529 (1953).

(33) C. E. Boozer and G. S. Hammond, *THIS JOURNAL*, **76**, 3861 (1954); G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3238 (1955).

roughly the same concentration as encountered in the chlorination products, were used to calibrate the procedure. The following calibration was found.

$$\frac{1.02(\text{area 2-chloro-})}{\text{area 1-chloro-}} = \frac{\text{mole 2-chloro-}}{\text{mole 1-chloro-}}$$

This equation was independent of the solvent used.

Analyses were performed by the injection of 10–20 μ l. (occasionally 30–40 μ l.) of chlorination product in the vapor fractometer. Since chlorination samples usually contained 0.005 mole of alkyl chloride per 25 ml., we were actually, in the case of a 10- μ l. sample, analyzing 2×10^{-6} mole of alkyl chloride. However, because of the extreme sensitivity of the method the precision of our results was good. In Table VI are some representative data which demonstrate our precision and also the effect of sample size. The analysis was completed by measuring the areas under the respective peaks by a planimeter with an experimental uncertainty in most cases of not more than 0.5%. For relative reactivities (t./p.) greater than 25 to 1, the experimental uncertainty increased considerably with an increase in relative reactivity.

TABLE VI
REPRESENTATIVE ANALYTICAL DATA

Sample no.	Sample size, μ l.	$\frac{\text{Area 2-chloro-}}{\text{Area 1-chloro-}}$
1	10	0.716
1	20	0.718
1	30	0.713
2	10	3.00
2	10	3.05
2	10	3.00

Chlorine analyses of the chlorination products were performed by treatment of an aliquot with an excess of sodium biphenyl reagent.⁴² After a 30-minute reaction period the reagent was destroyed with a large excess of alcohol and water and the entire mixture titrated potentiometrically with silver nitrate. When the organic phase interfered with this titration it was dispersed by the addition of Tergitol (non-ionic NPX). Hydrogen chloride evolved in the chlorinations was analyzed by potentiometric titration of the aqueous sodium hydroxide trap by silver ion. Blank corrections were applied.

Reagents.—Phillips research grade (>99.9 mole % pure) 2,3-dimethylbutane was used. Oxidation inhibitor was removed by passage over activated silica gel. The solvents used were of the highest purity commercially available. When deemed necessary they were distilled through a Vigreux column. When necessary solvents were dried by chromatographic filtration through silica gel.

Syntheses.—2-Chloro-2,3-dimethylbutane was prepared by the addition of hydrogen chloride to a NBS sample of tetramethylethylene (>99.9% pure). The material was distilled through a Podbielniak Heli-band column. The material used had a boiling point of 36° at 46 mm., n_D^{20} 1.4190. It was estimated to be 99.2% pure by GLC. The 1-isomer was not an impurity.

1-Chloro-2,3-dimethylbutane was prepared by the chlorination of 2,3-dimethylbutane. Chlorine (10 ml. of liquid at –35°) was used in the photochlorination of 40 ml. of 2,3-dimethylbutane at 25°. The resulting chlorination mixture was hydrolyzed by stirring with 100 ml. of water. Aqueous sodium hydroxide was added dropwise to maintain neutrality. Hydrogen chloride was no longer liberated after 48 hours of hydrolysis. The material was distilled in the Heli-band column. A sample, b.p. 124°, n_D^{20} 1.4235, was obtained which was free of the 2-isomer and estimated to be 95.5% pure by GLC.

t-Butyl-naphthalene was prepared by the alkylation of naphthalene with *t*-butyl alcohol in cyclohexane solution. The reactants (1 mole naphthalene, 1 mole *t*-butyl alcohol)

(*e.g.*, chlorosilanes, acetyl chloride) are passed through these columns at 80° then the column is so modified that it will quantitatively destroy the 2-chloro-2,3-dimethylbutane in a 10- μ l. sample of a 1% solution of 2-chloro-2,3-dimethylbutane. These same columns will also cause extensive dehydrohalogenation of *t*-butyl chloride at 80°. This behavior presumably is due to the formation of traces of Friedel-Crafts catalysts.

(42) L. M. Liggett, *Anal. Chem.*, **26**, 748 (1954).

in the presence of 100 ml. of cyclohexane were saturated with boron trifluoride at 25°. Distillation yielded 81 g. (0.44 mole) of a *t*-butyl-naphthalene, b.p. 100–105° at 4 mm., n_D^{20} 1.5746. This material is presumably the 2-isomer or possibly a mixture of isomers.⁴³

9-*n*-Butylanthracene.—Attempts to prepare 9-*t*-butylanthracene from *t*-butylmagnesium chloride and anthrone gave isobutylene and the magnesium salt of 9-anthrol. However, *n*-butylmagnesium chloride reacted with anthrone to give 9-*n*-butylanthracene. Anthrone (1 mole), as a slurry in benzene, was added to 1.5 moles of *n*-butylmagnesium chloride in ether. The mixture was stirred for 12 hours after which the ether was removed by distillation. The residue was treated with water and finally 20% hydrochloric acid. The benzene was removed by distillation to give a residue which was only partially soluble in ethanol at 80°. Crystallization of the ethanol-soluble material, twice from ethanol and once from 2,3-dimethylbutane, gave 30 g. (0.13 mole) of 9-*n*-butylanthracene, m.p. 42–45°. The material had a light yellow color.

2-Deuterio-2-methylbutane.—*t*-Butylmagnesium chloride was prepared in peroxide-free *n*-butyl ether. After preparation of the Grignard reagent in a large excess of ether (3 l. ether/mole of Grignard reagent) approximately one-third of the ether was removed by vacuum distillation at room temperature. The Grignard reagent was next neutralized with deuterium chloride prepared by the reaction of 99.8% deuterium oxide with benzoyl chloride.⁴⁴ The 2-deuterio-2-methylpropane was distilled into a Dry Ice receiver and rectified in a Podbielniak low temperature column (>100 plates). A constant boiling sample having constant thermal conductivity was collected. Analysis by mass spectrometry indicated the presence of 95% C₄H₉D and 5% C₄H₁₀.

Chlorination of 2-Deuterio-2-methylpropane.—The chlorination procedure was essentially that described for 2,3-dimethylbutane except that the reaction flask was immersed in an acetone-bath maintained at $-15 \pm 1^\circ$ by the addition of Dry Ice. Hydrogen-free nitrogen was dried by passage over glass beads coated with phosphorus pentoxide and the mixture of hydrogen and deuterium chlorides evolved was collected in a U-tube in a liquid oxygen trap. The system was protected from atmospheric moisture by another phosphorus pentoxide tube. After the chlorination was completed the mixture of hydrogen and deuterium chlorides was transferred to a Stock-type vacuum system by distillation from a methylcyclohexane bath (-126°) to a liquid nitrogen trap.⁴⁵ This distillation was repeated several times to completely remove traces of 2-methyl-2-deuteriopropane. A measured aliquot of the mixture of hydrogen and deuterium chlorides was added to a 100-fold excess of magnesium ribbon in a Pyrex tube which had been dehydrated by baking at 10^{-6} mm. for 24 hours at 500°. The tube was sealed off and heated at 500° for 24 hours. Analysis of the hydrogen-deuterium mixture was performed by opening a break-off tip of this tube and introducing the gases into a mass spectrometer at low pressures, to avoid the formation of H₃⁺.

t-Butyl and isobutyl chlorides were analyzed by GLC by using a 2-m. B-column of a Perkin-Elmer vapor fractometer. Calibration under our conditions indicated

$$\frac{1.02(\text{area } t\text{-butyl chloride})}{\text{area isobutyl chloride}} = \frac{\text{mole } t\text{-butyl chloride}}{\text{mole isobutyl chloride}}$$

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SCHENECTADY, N. Y.

(43) F. C. Whitmore and W. H. James, *THIS JOURNAL*, **65**, 2088 (1942).

(44) H. C. Brown and C. Groot, *ibid.*, **64**, 2223 (1942).

(45) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.