[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Solvent Effects in the Reactions of Free Radicals and Atoms. III. Effects of Solvents in the Competitive Photochlorination of Hydrocarbons and Their Derivatives[1]

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The relative reactivities of sixteen different carbon–hydrogen bonds toward a chlorine atom have been measured in the presence of aliphatic solvents, benzene, *t*-butylbenzene and carbon disulfide. A 50,000-fold range of reactivity is covered. The results support the conclusion that the reactivity of chlorine atoms can be greatly altered by interaction with the solvent. It is concluded that differences in reactivity of carbon–hydrogen bonds which are due to differences in the resonance stabilization of the incipient alkyl radicals can be greatly accentuated by the use of solvents that complex with the chlorine atom. However, differences in reactivity that are due solely to differences in the availability of electrons at the carbon–hydrogen bonds involved are not appreciably affected by solvents. The importance of polar effects and resonance effects in determining the reactivity of a carbon–hydrogen bond toward a chlorine atom are discussed.

In the preceding article the effects of a large number of solvents upon the position of attack of a chlorine atom upon 2,3-dimethylbutane were measured.[2] We have selected three appropriate solvents, benzene, *t*-butylbenzene and carbon disulfide, and in their presence have measured the relative reactivities of sixteen different carbon–hydrogen bonds toward a chlorine atom. The reactivities of these carbon–hydrogen bonds also have been compared in the presence of aliphatic solvents.

The reactivities of carbon–hydrogen bonds toward a chlorine atom are usually explained by a combination of polar and resonance effects.[3] Furthermore, it has been suggested that resonance effects are not particularly important in this reaction because the carbon–hydrogen is only partly (*ca.* 10%) broken in the transition state for the attack of the very reactive chlorine atom upon most carbon–hydrogen bonds.[4] In terms of the transition state for the reaction

$$X\cdot + RH \longrightarrow \underset{I}{[R{:}H\cdot X} \longleftrightarrow \underset{II}{R^{+}\cdot H\,X{:}^{-}} \longleftrightarrow R\cdot\,H{:}X] \longrightarrow R\cdot + HX$$

structure III, involving extensive rupture of the carbon–hydrogen bond, is not very important when X is chlorine.

The polar effect, wherein chlorine atoms preferentially attack carbon–hydrogen bonds with the highest electron density, can be explained by either structure I or II. Structure II, originally proposed by Mayo and Walling,[5] should be most important when X· has a high electron affinity and when the carbon–hydrogen bond in question has the highest availability of electrons. A polar effect may also be expected even when there is very little breaking of the carbon–hydrogen bond in the transition state. Structure I, representing such a transition state, may be considered to involve a weak attraction between the electrophilic chlorine atom and the electron pair of the carbon–hydrogen bond.

In terms of the Hammond postulate,[6] when X· is very reactive the transition state will resemble the reactants (best described by I) while when the reactivity of X· is low, the stability of the products becomes important in determining reactivity and the transition state resembles the products of the reaction. The effect of solvents upon the position of attack of chlorine atoms upon 2,3-dimethylbutane[2] can be explained as a change in transition state from one resembling reactants for attack by a free chlorine atom to one more closely resembling products when the chlorine atom is complexed by an appropriate solvent. However, this interpretation raises the question of whether solvents affect mainly the magnitude of the polar effect or the magnitude of the resonance stabilization of the incipient free radicals. It was with this question in mind that the data summarized in the following section were determined.

Results and Discussion

Procedure.—The results of numerous competitive chlorinations are summarized in Table I. In nearly all cases a large excess of the hydrocarbon or mixture of hydrocarbons was photochlorinated and the products analyzed by gas–liquid chromatography (GLC). The analysis was calibrated by the use of prepared samples of the pure alkyl chlorides. The reactivity of t.-butylbenzene relative to cycloöctane toward the "free" chlorine atom was determined by competitively chlorinating approximately 0.005 mole of a mixture of the hydrocarbons in 25 ml. of carbon tetrachloride with 0.005 mole of chlorine. The decreases in concentrations of the two hydrocarbons were measured by GLC and the relative reactivities (per hydrogen atom) determined by the equation

$$\text{rel. react.}\left[\frac{C_8H_{16}}{C_6H_5C(CH_3)_3}\right] = \frac{9}{16}\,\frac{\log [C_8H_{16}]_i - \log [C_8H_{16}]_f}{\log [C_{10}H_{14}]_i - \log [C_{10}H_{14}]_f}$$

where the subscripts refer to initial and final concentrations. It should be noted that polychlorination does not interfere with this type of an analysis. The relative reactivities of toluene and cyclohexane toward a chlorine atom in an aliphatic solvent were obtained by competitive chlorination at a number of toluene concentrations and extrapolation to zero toluene concentration (see Table II).

(1) Directive Effects in Aliphatic Substitutions. XII. Presented before the Division of Organic Chemistry at the New York City Meeting of the American Chemical Society, September, 1957.

(2) G. A. Russell, THIS JOURNAL, **80**, 4987 (1958).

(3) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 352.

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

(5) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

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

TABLE I

RELATIVE REACTIVITIES OF VARIOUS CARBON–HYDROGEN BONDS TOWARD CHLORINE ATOMS

Hydrocarbon	Temp., °C.	Hydrogen	Relative reactivity: "Free" Cl	Complexed chlorine atom: 4.0 *M* C_6H_6	Complexed chlorine atom: 4.0 *M* $C_6H_5C(CH_3)_3$	Complexed chlorine atom: 12 *M* CS_2
2,3-Dimethylbutane	25	1°	1.0[a]	1.0[a]	1.0[a]	1.0[a]
		3°	4.2	20	35	225
n-Pentane[b]	25	1°	0.97	0.97	0.92	0.86
		2°	3.6	4.6	6.2	25
Tetramethylsilane	25	1°	1.1	..	1.1	0.96
Trimethylchlorosilane	25	1°	0.17	0.16	0.16	0.20
2,3-Dimethylbutane	40	1°	1.0[a]	1.0[a]	1.0[a]	1.0[a]
		3°	3.9	16	29.5	200
Cyclopentane	40	2°	2.8	5.2	7.3	23
Cyclohexane	40	2°	2.7	5.2	6.9	20
Cycloheptane	40	2°	3.0	6.4	10	40
Cyclooctane	40	2°	4.3	9.2	16	75
t-Butyl chloride	40	1°	0.12	0.10	0.16	0.22
t-Butylbenzene	40	1°	.63	..	.60	..
Methylene chloride	40	2°	.011	..	.030	0.044
Chloroform	40	3°	.0051	..	.017	0.033
Toluene	40	1°	1.1–1.2	2.1	2.8	11
Acetonitrile	40	1°	0.004	0.003	..	.003

[a] Assumed. [b] s.-Hydrogen atom at the 2- and 3-position assumed to have the same reactivity.

Relative Reactivities in Aliphatic Solvents.—Table I demonstrates the well known reactivity sequence of carbon–hydrogen bonds of t. > s. > p.[4,7] However, this reactivity sequence is only a first approximation which fails when negatively substituted hydrocarbons, such as chloroform, are considered. The reactivity sequence of carbon–hydrogen bonds in a branched-chain hydrocarbon of t. > s. > p. usually has been interpreted in terms of the resonance stabilization of the alkyl free radicals. However, this reactivity sequence can also be explained solely on the basis of inductive effects,[8] the availability of electrons increasing from prim.- to sec.- to tert.-carbon–hydrogen bonds.

The reactivities of the hydrogen atoms of the cycloalkanes, on the basis of either resonance structure II or III, are expected to follow the sequence $C_8 > C_7 > C_5 > C_6$.[8] The observed relative reactivities of the cycloalkanes indicate that a free chlorine atom is so reactive that small differences in stabilities of the resulting alkyl free radicals do not have an appreciable effect on the relative reactivities. A similar conclusion was reached previously in regard to the effect of steric strain in the reactions of chlorine atoms with branched-chain hydrocarbons.[4]

The methyl groups of 2,3-dimethylbutane, tetramethylsilane and *n*-pentane all have nearly the same reactivity toward a chlorine atom. However, the methyl groups of trimethylchlorosilane and *t*-butyl chloride are only about 0.2 and 0.1 as reactive. Here the inductive effect of the chlorine substituent has decreased reactivity nearly 5- to 10-fold. The methyl group of acetonitrile is only 0.004 as reactive as a methyl group of an aliphatic hydrocarbon, presumably because of the pronounced electron-withdrawing properties of a cyano group.

Further examples of the importance of the polar effect are the relative reactivities of the hydrogen atoms of methylene chloride and chloroform. Toward a chlorine atom, methylene chloride is only 0.004 as reactive as a methylene group of cyclohexane. The chloroform hydrogen atom is even less reactive. Even though the trichloromethyl radical is considered to be about as stable as an ordinary t.-alkyl radical,[9] the hydrogen atom of chloroform is only about 0.001 as reactive as the t.-hydrogen atom of 2,3-dimethylbutane.

The p.-hydrogen atoms of toluene are surprisingly no more reactive than the p.-hydrogen atoms of an aliphatic hydrocarbon. We have considered the anomalous reactivity of toluene previously and attributed it to the fact that the electron-withdrawing power of the phenyl ring offsets the increased reactivity expected because of the resonance stabilization of the benzyl radical.[10] As noted by Van Helden and Kooyman,[11] the inductive effect of a phenyl group is even apparent in the β-position; the p.-hydrogen atoms of *t*-butylbenzene are only 0.6 as reactive as the p.-hydrogen atoms of an aliphatic hydrocarbon.

The present results indicate little difference in energy of activation for the attack of chlorine atoms upon cyclohexane and toluene, at least in the presence of 8 *M* toluene.

The data of Table II indicate that *PZ* term of the Arrhenius equation favors attack of a chlorine atom upon a cyclohexane hydrogen atom by a factor of about 2.3. Thus, although a chlorine atom has the same energy of activation for reaction with a toluene or a cyclohexane hydrogen atom, cyclohexane is attacked 9.2 times as readily as toluene. The discrepancy between 9.2 and the ratio of reac-

(7) H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935); **28**, 333 (1936).

(8) (a) H. C. Brown, R. S. Fletcher and R. B. Johannesen, THIS JOURNAL, **73**, 212 (1951); (b) C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker and J. Herbert, *ibid.*, **75**, 2078 (1953).

(9) The bond dissociation energies are CCl_3–H, 90; $(CH_3)_3C$–H, 89 kcal. mole^{-1}, T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, Inc., New York, N. Y., 1954, p. 272.

(10) G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4578 (1955).

(11) R. Van Helden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954)

TABLE II

EFFECT OF TEMPERATURE AND TOLUENE CONCENTRATION ON THE PRODUCTS OF THE COMPETITIVE CHLORINATION OF CYCLOHEXANE AND TOLUENE

Temp., °C.	Toluene concn.[a]	Rel. react. ($C_6H_{12}/C_6H_5CH_3$)[b]
25	8.0	2.72
40	8.0	2.84
55	8.0	2.52
80	7	2.80[c]
40	4.0	2.67
40	2.0	2.52
40	0	2.3–2.4[d]
70	Vapor phase	2.12[e]

[a] Mole liter^{-1}. [b] Relative reactivity per hydrogen atom. [c] Ref. 3a. [d] By extrapolation. [e] Ref. 3d.

tive hydrogen atoms in cyclohexane and toluene indicates a weakness in assigning statistical factors based on the number of hydrogen atoms in computing relative reactivities. The finding that cyclohexane and toluene possess equal energies of activation for reaction with chlorine atoms in no way vitiates the conclusion that toluene has an anomalous reactivity, since, on the basis of benzyl-type resonance, a much lower energy of activation for attack on toluene would have been expected.[12] Bromine atoms do indeed attack toluene many times more readily than they attack cyclohexane.[10]

Polar Effects in Complexing Solvents.—To observe the effect of solvent upon the deactivation of carbon–hydrogen bonds by electron-withdrawing substituents, we obtained measurements of the relative reactivities of compounds capable of giving alkyl radicals with the same amounts of resonance stabilization but having widely different reactivities due to the polar effect. Comparison of the relative reactivity of the primary hydrogen atoms of tetramethylsilane and trimethylchlorosilane in the absence of a complexing solvent, and in the presence of 4 *M* benzene, 4 *M* *t*-butylbenzene or 12 *M* carbon disulfide, indicates little effect of solvent upon relative reactivity (Table I). When the reactivity of the p.-hydrogen atom of *t*-butyl chloride is compared with the reactivity of a p.-hydrogen atom of 2,3-dimethylbutane, a small solvent effect is observable. In an aliphatic solvent the primary hydrogen atom of 2,3-dimethylbutane is 8 times as reactive as the hydrogen atom of *t*-butyl chloride. This ratio decreases to 6-fold in 4 *M* *t*-butylbenzene and to 4.5-fold in 12 *M* carbon disulfide. The relative reactivities of the p.-hydrogen atom of 2,3-dimethylbutane and acetonitrile again indicate little solvent effect. A p.-hydrogen atom of 2,3-dimethylbutane is 250–350 times as reactive as a hydrogen atom of acetonitrile in either an aliphatic solvent or in the presence of 12 *M* carbon disulfide. Similarly, a p.-hydrogen atom of *t*-butylbenzene is 0.63 times as reactive as a p.-hydrogen atom of 2,3-dimethylbutane in the presence of carbon tetrachloride, while in the presence of 4 *M* *t*-butylbenzene the relative reactivities are 0.60 to 1. All of these results suggest that when the relative reactivities of two hydrogen atoms toward a chlorine atom are determined by the electron densities of the carbon–hydrogen bonds involved, the relative reactivities are affected only slightly by solvents.

Walling and Miller have discussed effects of solvents in hydrogen abstraction reactions where relative reactivities are determined by a polar effect.[13] Solvation should decrease the effective electron affinity of a chlorine atom. This effect, by itself, should reduce the magnitude of the polar effect by de-emphasizing resonance Structure II.[13] On the other hand, solvation of the chlorine atom will decrease its reactivity and lead to a transition state involving a greater degree of bond breaking. This effect, by itself, should increase the importance of both resonance forms II and III in the transition state. Experimentally we have observed little solvent effect on relative reactivities determined solely by polar effects. Possibly the effect of decreased electron affinity of the chlorine atom in the presence of complexing solvents is counter-balanced by the increased importance of resonance stabilization of the transition state.

Resonance Effects in Complexing Solvents.—As the solvent is changed from an aliphatic solvent to 4 *M* benzene to 4 *M* *t*-butylbenzene to 12 *M* carbon disulfide, the relative reactivities (t./p.) of the hydrogen atoms of 2,3-dimethylbutane at 25° increase from 4.2 to 20 to 35 to 225. Similarly, the relative reactivities (s./p.) of the hydrogen atoms of *n*-pentane increase from 3.0 to 4.9 to 6.8 to 29. Thus, the same trend is observed in the relative reactivities of p.- and s.-hydrogens as in the case of p.- and t.-hydrogen atoms. We have previously argued that differences in reactivity due to differences in the electron density of the carbon–hydrogen bonds involved are not appreciably affected by solvents. Therefore, the large solvent effects noted in the chlorination of *n*-pentane and 2,3-dimethylbutane are most likely due to the resonance stabilization of the incipient alkyl radicals. As the chlorine atom becomes complexed its reactivity decreases and the degree of bond-breaking in the transition state for attack on a carbon–hydrogen bond increases. With an increase in bond-breaking, resonance stabilization of the incipient free radical (resonance form III) becomes more important and differences in reactivity due to differences in the resonance stabilization of the alkyl radicals increase. Previously we mentioned that the reactivity sequence for hydrogen atoms, t. > s. > p., could be explained on a strictly inductive basis in terms of the availability of electrons in the carbon–hydrogen bonds involved. The effects of solvents upon the relative reactivities of p.-, s.- and t.-hydrogen atoms is strong evidence that resonance stabilization of alkyl radicals is also an important factor in determining this reactivity sequence.

Until now it has been impossible to separate complementing effects due to the stability of alkyl radicals from effects due to electron availability in the reactions of chlorine atoms with carbon–hydrogen bonds. The present results suggest that such a separation can be made, at least qualita-

(12) From the data of Table I, we are able to state that the reactivity of cyclohexane hydrogen atoms is not anomalous since these s.-hydrogen atoms have nearly the same reactivity as s.-hydrogen atoms in an aliphatic molecule such as *n*-pentane.

(13) C. Walling and B. Miller, THIS JOURNAL, **79**, 4181 (1937).

tively, from the magnitude of the solvent effect—*relative reactivities that are determined mainly by the availability of electrons in the carbon–hydrogen bond are not particularly sensitive to solvent effects while relative reactivities that are determined mainly by the stabilities of the incipient free radicals are very sensitive to changes in solvent.*

The relationship between solvent effect and radical stability is further confirmed when the relative reactivities of the cycloalkanes toward chlorine atoms are considered. The relative stabilities of cycloalkyl radicals are believed to be $C_8H_{15} > C_7H_{13} > C_5H_9 > C_6H_{11}$.[8b] However, in an aliphatic solvent, this reactivity sequence is only partially confirmed; $C_8:C_7:C_5:C_6 = 1.5:1.0:1.0:1.0$. In 4 *M* benzene the sequence is $C_8:C_7:C_5:C_6 = 1.8:1.2:1.0:1.0$ while in 4 *M* *t*-butylbenzene the full I-strain pattern[8a] is revealed, $C_8:C_7:C_5:C_6 = 2.3:1.5:1.1:1.0$. In 12 *M* carbon disulfide these reactivity differences are accentuated, $C_8:C_7:C_5:C_6 = 3.8:2.0:1.2:1.0$. Again our explanation is that as the chlorine atom becomes complexed and its reactivity is reduced, the resonance stabilization of the incipient alkyl radicals becomes more important and reactivity follows the stability of the alkyl radicals more closely.

So far all examples of the effect of complexing solvents upon the resonance effect have been to accentuate reactivity differences. Presumably this will always be the case when reactivity is determined solely by the resonance stabilization of the incipient alkyl radicals. However, when reactivities are determined by a combination of resonance and polar effects, complexing solvents may cause the relative reactivities to actually become more nearly equal. Consider the relative reactivities of the hydrogen atom of chloroform and the p.-hydrogen atom of 2,3-dimethylbutane. Despite the fact that the carbon–hydrogen bond in chloroform is weaker than a primary carbon–hydrogen bond in an alkane,[9] the chloroform hydrogen atom is considerably less reactive (1 to 200) in aliphatic solvents than the p.-hydrogen of 2,3-dimethylbutane because of the polar effect. In 4 *M* *t*-butylbenzene this reactivity difference is 1 to 60, while in 12 *M* carbon disulfide the relative reactivities are 1 to 30. A similar effect is observed when the reactivity of the hydrogen atoms of methylene chloride and the p.-hydrogen atoms of 2,3-dimethylbutane are considered. In these cases, the effect of solvents is to increase the importance of resonance stabilization of the incipient alkyl radical in determining relative reactivity and by doing so to decrease the importance of the polar effect in determining reactivity.

The effect of solvents upon the reactivity of toluene can be interpreted in a similar manner. In aliphatic solvents, a toluene hydrogen atom and a p.-hydrogen atom of 2,3-dimethylbutane have nearly equal reactivity even though the benzyl radical is known to have much greater resonance stabilization than an *n*-alkyl radical. Here the unusually low reactivity of toluene has been ascribed to the electron-withdrawing properties of the phenyl ring.[10] As the solvent is changed to 4 *M* benzene to 4 *M* *t*-butylbenzene to 12 *M* carbon disulfide, the reactivity of toluene increases to 2.1, 2.8 and finally to 11 times the reactivity of the p.-hydrogen atoms of 2,3-dimethylbutane. Again, the effect of these solvents is to increase the importance of resonance stabilization and to minimize the polar effect.

Although the data of Table I have, in all cases, qualitatively confirmed our viewpoint in regard to resonance and polar effects controlling the reactivity of carbon–hydrogen bonds, it has nevertheless been somewhat disappointing from a quantitative aspect. For example, when the resonance effect is controlling, as in the reaction of bromine atoms, a toluene hydrogen atom is many times more reactive than a cyclohexane hydrogen atom.[10] If solvation of a chlorine atom could reduce its reactivity to a point where it resembles a bromine atom, we would expect this solvated chlorine atom to attack toluene in preference to cyclohexane. Actually, even in 12 *M* carbon disulfide, a cyclohexane carbon–hydrogen bond is still twice as reactive as a toluene carbon–hydrogen bond toward a chlorine atom. Admittedly the reactivity of a toluene hydrogen atom relative to a cyclohexane hydrogen atom has increased from 0.40:1 in aliphatic solvents to 0.55:1 in 12 *M* carbon disulfide, but we apparently are still a long way from a solvated chlorine atom which has a reactivity approaching that of a bromine atom. In the chlorination of 2,3-dimethylbutane, ethyl iodide appeared to be one of the most selective solvents. We, therefore, competitively chlorinated toluene and cyclohexane in the presence of 4 *M* ethyl iodide. The results were again complicated by the formation of iodine. The alkyl chlorides were formed in a ratio which suggested that a toluene hydrogen atom is 1.8 times as reactive as a hydrogen atom of cyclohexane. However, we are unable to state that the alkyl chlorides found are representative of the point of attack of a chlorine atom upon the hydrocarbons, although we have no evidence to the contrary.

Experimental

Analysis of Chlorination Mixtures.—The chlorination procedure and apparatus already have been described.[2] Analyses of the chlorination products were performed by GLC using a Perkin–Elmer model 154B vapor fractometer. In all cases analytical procedures were calibrated by the use of prepared samples of the alkyl chlorides. Pertinent data concerning analysis and calibrations are summarized in Table III.

The analysis of the chlorination products of *n*-pentane in the presence and absence of 2,3-dimethylbutane presented some complications. The 2- and 3-chloropentanes were not separated in the column used for analysis although they obviously could have been separated by use of a longer column. Instead, the areas under the unresolved peak were measured and relative reactivities calculated on the basis that the 2- and 3-hydrogen atoms had the same reactivity. It also was assumed that 2- and 3-chloropentane had equal retention volumes.

Competitive chlorination of *n*-pentane with 2,3-dimethylbutane had the additional drawback that the retention times for 1-chloropentane and 2-chloro-2,3-dimethylbutane were identical. However, from the area of the peak for 2- and 3-chloropentane the expected area for the 1-chloropentane peak could be calculated. Also, from the area of the 1-chloro-2,3-dimethylbutane peak the expected area of the 2-chloro-2,3-dimethylbutane could be obtained. For example, in a competitive chlorination of *n*-pentane and 2,3-dimethylbutane it was found that the peak area correspond-

TABLE III

CALIBRATION FACTORS FOR GAS–LIQUID CHROMATOGRAPHY OF ALKYL CHLORIDES

Compd. A	Compd. B	Temp., °C.	Column[a]	Relative Retention Times A	Relative Retention Times B	Correction factor[b]
2-Chloro-2,3-dimethylbutane	1-Chloro-2,3-dimethylbutane	80	2 m. B	1.0	1.45	1.02
1-Chloro-2,3-dimethylbutane	1-Chloropentane	80	2 m. B	1.45	1.0	1.035
1-Chloro-2,3-dimethylbutane	Chloromethyltrimethylsilane	80	2 m. B	1.45	0.61	1.10
1-Chloro-2,3-dimethylbutane	Chloromethyldimethylchlorosilane	80	2 m. A	1.45	1.12	1.521
2-Chloro-2,3-dimethylbutane	Chlorocyclopentane	80	2 m. B	1.0	1.25	0.917
Chlorocyclopentane	Chlorocyclohexane	120	2 m. B	1.0	2.04	1.07
Chlorocyclohexane	Chlorocycloheptane	120	2 m. B	2.04	4.9	1.02
Chlorocyclohexane	Chlorocycloöctane	100	2 m. K	1.0	4.65	0.79
Chlorocyclohexane	Benzyl chloride	150	2 m. B	1.0	2.47	1.045
Chlorocyclopentane	1,2-Dichloro-2-methylpropane	80	2 m. B	1.25	1.06	0.98
Chloroform	1,2-Dichloro-2-methylpropane	80	2 m. B	0.525	1.06	0.877
Carbon tetrachloride	1,2-Dichloro-2-methylpropane	80	2 m. B, 2 m. K	1.0	2.25	1.01
Chloroacetonitrile	1,2-Dichloro-2-methylpropane	80	2 m. B	1.36	1.06	1.39
Chlorocycloöctane	Neophyl chloride	120	2 m. K	4.65	14.4	1.21

[a] Perkin–Elmer Corp., Norwalk, Conn. [b] (Area A/area B) correction factor = mole A/mole B.

ing to 2- and 3-chloropentane was 198 units, for 1-chloro-2,3-dimethylbutane 51 units and for 2-chloro-2,3-dimethylbutane and 1-chloropentane 107 units. From the data obtained in the chlorination of *n*-pentane alone, and 2,3-dimethylbutane alone, it was calculated that the peak area for 1-chloropentane should be 68 units and for 2-chloro-2,3-dimethylbutane should be 36 units. The sum of these calculated values, 104 units, agrees favorably with the experimental value of 107 units.

Reagents.—Phillips research grade (>99.9% pure) 2,3-dimethylbutane, *n*-pentane, cyclopentane and cyclohexane were used. The *t*-butylbenzene and toluene used were Phillips 99 mole % minimum. Cycloheptane (Madison Laboratories) was rectified in a 20-plate helices-packed column and by GLC had a purity of >99.9%. Cycloöctane was prepared by the catalytic reduction of commercial cyclooctatetraene and rectified in the packed column. Its purity was indicated to be 99.5% by GLC. A sample of tetramethylsilane of unknown origin had a purity by GLC of 99.9%. Trimethylchlorosilane was prepared from hexamethylsilane and aluminum chloride and had a purity by GLC of 96%. Eastman Kodak Co. methylene chloride and chloroform were rectified in the packed column. The chloroform was free of ethanol as judged by GLC. Acetonitrile (C.P., Fisher) was chromatographically filtered over activated silica gel. The *t*-butyl chloride was estimated to be 99% pure by GLC.

Reference Compounds.—Calibration of the GLC analyses required a variety of alkyl chlorides of known purity. The 1- and 2-chloro-2,3-dimethylbutanes already have been described. Eastman Kodak Co. benzyl chloride, chlorocyclohexane and chloroacetonitrile had purities of 100.0% by GLC after distillation. Chlorocyclopentane obtained from Columbia Chem. Co. was rectified in the packed column to give material judged to be 100.0% pure by GLC. Chloromethyltrimethylsilane, prepared by the chlorination of tetramethylsilane, had a purity of 99.8%. Chloromethyldimethylchlorosilane, Pennisular Chem. Research, Inc., having a purity of 95.0% was used. 1-Chloropentane, prepared from *n*-amyl alcohol,[14] was 99.3% pure. Chlorocycloheptane was prepared by the chlorination of cycloheptane and then rectification in a Podbielniak Heli-band column. The sample had a purity of 97.0%. Chlorocycloöctane was prepared by the chlorination of cycloöctane. Distillation through a short Vigreux column at 28.5 mm. gave a fraction boiling at 115–120°, $n^{20}D$ 1.4880, that was judged to be 99.0% pure by GLC. Neophyl chloride prepared by the chlorination of *t*-butylbenzene had a b.p. of 110–112° at 19 mm., $n^{20}D$ 1.5259, and an indicated purity of 95.5%. 1,2-Dichloro-2-methylpropane was prepared by the chlorination of *t*-butyl chloride. Material boiling at 106–108°, $n^{20}D$ 1.4370, had a purity of 98.0%. None of the impurities detected in these compounds had a retention time which would cause an interference with the other alkyl chloride used in the calibration (see Table III). When used as standards for analysis these materials were corrected for the presence of impurities.

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SCHENECTADY, N. Y.

(14) F. C. Whitmore, F. A. Karnatz and A. H. Popkin, THIS JOURNAL, **60**, 2540 (1938).