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Homolytic Chlorination of Aliphatic Compounds. IV.[1] Chlorination of Chloroalkanes by *t*-Butyl Hypochlorite

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Chlorination of chloroalkanes by *t*-butyl hypochlorite was investigated by means of competitive experiment. Relative reactivities thus obtained were compared with those toward hydrogen abstraction by *t*-butoxy radicals derived from other sources. From the results it was concluded that a main chain carrier of this chlorination was a *t*-butoxy radical. Structure-reactivity relationships in *t*-butyl hypochlorite chlorination were also investigated. Linear free energy relationship was found to exist between the reactivities of methyl hydrogen of CH_3-X and Taft's σ^* constants for the substituent X,$\rho^* = -0.69$. α-Chlorine substituents were found always to enhance the rate of hydrogen abstraction of this position. Resonance effects of α-chlorine substituent is considered to be more important than in photochlorination with chlorine.

Chemistry of aliphatic chlorination by *t*-butyl hypochlorite has been extensively investigated by Walling and his co-workers.[2] They proposed a radical chain mechanism involving hydrogen abstraction by a *t*-butoxy radical, on the basis of the selectivity of the reaction being parallel to that of hydrogen abstraction by *t*-butoxy radicals derived from other sources.[3] Gilliom and Ward[4] reported ρ value (with σ) to be -0.75 for benzylic chlorination by *t*-butyl hypochlorite at 40°C. This value is quite different from that obtained by Sakurai and Hosomi[5] (with σ^+, -0.32 at 45°C) for benzylic hydrogen abstraction by *t*-butoxy radical derived from di-*t*-butyl peroxalate, and is rather similar to ρ value for chlorination by chlorine.[6] Thus it seems that benzylic chlorination by *t*-butyl hypochlorite involves a chlorine atom, rather than *t*-butoxy radical, as a chain carrier. Recently Walling and McGuiness[7] gave some evidence for the mechanism of benzylic chlorination by *t*-butyl hypochlorite.

We have been investigating substituent effects on the reactivities of aliphatic compounds toward a chlorine atom. A linear free energy relationship has been found to exist between the reactivity of CH_3–X and the σ^* value of X.[8] The study was extended to *t*-butyl hypochlorite chlorination. In this paper we wish to present an evidence which indicates that a main chain carrier of *t*-butyl hypochlorite chlorination of chloroalkanes is *t*-butoxy radical, in order to compare structure-reactivity relationship in this chlorination with that in photochlorination by chlorine.

Results and Discussion

***t*-Butoxy Radical as a Chain Carrier.** Three possible chain carriers can be considered for the *t*-butyl hypochlorite chlorination.

$$\begin{array}{ll}
\text{scheme 1} & t\text{-BuOCl} \xrightarrow{h\nu} t\text{-BuO}\cdot + \text{Cl}\cdot \\
 & t\text{-BuO}\cdot + \text{RH} \longrightarrow t\text{-BuOH} + \text{R}\cdot \\
 & \text{R}\cdot + t\text{-BuOCl} \longrightarrow \text{RCl} + t\text{-BuO}\cdot \\
\text{scheme 2} & t\text{-BuOCl} + \text{HCl} \rightleftarrows \text{Cl}_2 + t\text{-BuOH} \\
 & \text{R}\cdot + \text{Cl}_2 \longrightarrow \text{RCl} + \text{Cl}\cdot \\
 & \text{Cl}\cdot + \text{RH} \longrightarrow \text{HCl} + \text{R}\cdot \\
\text{scheme 3} & t\text{-BuO}\cdot \longrightarrow \text{CH}_3\text{COCH}_3 + \text{CH}_3\cdot \\
 & \text{CH}_3\cdot + \text{RH} \longrightarrow \text{CH}_4 + \text{R}\cdot
\end{array}$$

Scheme 1 is a mechanism proposed originally by Walling,[2] which involves a *t*-butoxy radical as a chain carrier. In scheme 2, an actual chlorinating agent is chlorine molecule which is derived by a reversible reaction of *t*-butyl hypochlorite with hydrogen chloride formed through the subsequent chain steps involving a chlorine atom as a hydrogen abstracting species. The third possible chain carrier is a methyl radical which is formed by decomposition of *t*-butoxy radical (scheme 3). *t*-Butyl

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[1] Part III: M. Kosugi, K. Takeuchi and T. Migita, This Bulletin, **42**, 3354 (1969).

[2] C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, **82**, 6108, 6113 (1960); C. Walling " Free Radicals in Solution," I. U. P. A. C. (1967), p. 69.

[3] C. Walling and A. Padwa, *J. Org. Chem.*, **27**, 2979 (1962).

[4] R. D. Gilliom and D. F. Ward Jr., *J. Amer. Chem. Soc.*, **87**, 3944 (1965).

[5] H. Sakurai and A. Hosomi, *ibid.*, **89**, 458 (1967).

[6] G. A. Russell and R. C. Williamson, *ibid.*, **86**, 2357 (1964).

[7] C. Walling and J. A. McGuiness, *ibid.*, **91**, 2053 (1969).

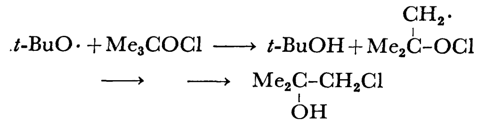
[8] T. Migita, M. Kosugi, Y. Tanaka and Y. Nagai, *Yuki Gosei Kagaku Kyokai Shi.*, **25**, 908 (1967).

hypochlorite reacted with chloroalkanes under irradiation by 500 W tungsten lamp, giving chlorinated products and *t*-butyl alcohol as main products. Relative amounts of these products are shown in Table 1. The results eliminate the possibility of scheme 3, since formation of *t*-butyl alcohol can not be expected from this mechanism.

Table 1. Ratio of chloride and *t*-butyl alcohol (40°)

(RH)	(RCl)/(*t*-BuOH)
CH_2ClCH_2Cl	1.05
$CHCl_3$	1.00
$(CH_3)_3CCl$	0.90
CH_2Cl_2	0.74
$(CH_3)_2CCl_2$	0.35

Table 1 shows that chlorination of 1,2-dichloroethane, chloroform gave the chlorinated product and *t*-butyl alcohol in equimolar amount. This is in agreement with the product pattern from the reaction schemes 1 and 2. However, less amounts of chlorinated products compared with *t*-butyl alcohol were formed from the chlorination of 2,2-dichloropropane and methylene chloride. In these cases, vapor-phase chromatographic analysis of the reaction mixtures showed the presence of considerable amounts of an additional common product, which was identified to be 1-chloro-2-methyl-2-propanol. Walling and Padwa[9] reported the formation of this compound in decomposition of *t*-butyl hypochlorite in carbon tetrachloride solution, and proposed the formation path way as follows:

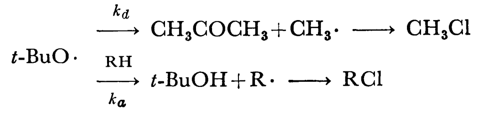


$$t\text{-BuO}\cdot + \text{Me}_3\text{COCl} \longrightarrow t\text{-BuOH} + \text{Me}_2\overset{\text{CH}_2\cdot}{\text{C}}\text{-OCl} \longrightarrow \longrightarrow \text{Me}_2\underset{\text{OH}}{\text{C}}\text{-CH}_2\text{Cl}$$

As will be seen later, while 1,2-dichloroethane and chloroform are relatively reactive substrates toward hydrogen abstraction by *t*-butoxy radical, 2,2-dichloropropane and methylene chloride are less reactive, so that *t*-butoxy radicals may abstract hydrogen atoms from *t*-butyl hypochlorite as well as from substrate molecules, forming *t*-butyl alcohol in a larger amount than chlorinated products.

In order to check the two possibilities of schemes 1 and 2, relative reactivities of several substrates towards the hypochlorite chlorination were compared with those towards hydrogen abstraction by *t*-butoxy radical derived from di-*t*-butyl peroxide.

Relative reactivities toward the chlorination were calculated from the relative yields of the chlorinated products from competitive reaction with binary mixtures of substrates. The relative reactivities towards *t*-butoxy radical formed by the photo-induced decomposition of di-*t*-butyl peroxide (high pressure mercury lamp) and *t*-butyl hypochlorite (tungsten lamp) were calculated from k_a/k_d derived from the relative yields of *t*-butyl alcohol and acetone formed by the following competition.[10]



$$t\text{-BuO}\cdot \begin{array}{l} \xrightarrow{k_d} \text{CH}_3\text{COCH}_3 + \text{CH}_3\cdot \longrightarrow \text{CH}_3\text{Cl} \\ \xrightarrow[k_a]{\text{RH}} t\text{-BuOH} + \text{R}\cdot \longrightarrow \text{RCl} \end{array}$$

Relatively reactive chloroalkanes were chosen as substrates, in order to avoid the hydrogen abstraction from a *t*-butoxy radical sources, which would result in overestimation of the rates of hydrogen abstraction from substrate molecules. The results are shown in Table 2.

Apparently, relative reactivities obtained from competitive chlorination with *t*-butyl hypochlorite are very close to those from di-*t*-butyl peroxide and quite different from those for photochlorination by chlorine. We can conclude that *t*-butoxy radical is the most important chain carrier in *t*-butyl hypochlorite chlorination of chloroalkanes.

Relative Reactivities of Chloroalkanes. Relative reactivities of chloroalkanes toward *t*-butoxy radical were determined by competitive chlorination with *t*-butyl hypochlorite, and were formed as shown in Table 3.

As expected from the electron-seeking nature of *t*-butoxy radicals,[2] reaction rates are affected by the polar nature of the substituents in the substrates.

Table 2. Relative reactivities of chloroalkanes

Substrate	Reagents			
	t-BuOCl Competitive chlorination	*t*-BuOCl Relative value of k_a/k_d	*t*-BuOOBu-*t* Relative value of k_a/k_d	Cl_2[11] Competitive chlorination
CH_2ClCH_2Cl	1.00 standard	1.00 standard	1.00 standard	1.00 standard
CCl_3CH_2Cl	0.86	0.74	0.84	0.02
$CHCl_2CHCl_2$	3.5	2.4	2.1	0.04
	(40°)	(40°)	(20—23°)	(40°)

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[9] C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, **85**, 1593 (1963).

[10] A. L. Williams, E. A. Oberright and J. W. Brooks, *ibid.*, **78**, 1190 (1956).

Table 3. Relative reactivities of chloroalkanes (40°C)

Reaction site	Substituent	*t*-BuOCl	Cl_2
CH_3-	-CH_2CMe_3	10.7	44
	-$CH_2CH_2CH_2Cl$	12.7	—
	-CH_2CH_2Cl	9.0	21
	-CMe_2Cl	4.2	9.8
	-CMeHCl	3.6	9.9
	-$CMeClCH_2Cl$	2.1	3.4
	-$CHClCH_2Cl$	2.3	3.3
	-$CMeCl_2$	1.00 (standard)	1.00 (standard)
	-CCl_3	0.12	0.07
CH_2Cl-	-$CH_2CH_2CH_3$	43.2	—
	-CH_2CH_3	31.6	18
	-$CH_2CH_2CH_2Cl$	27.3	—
	-CH_2CH_2Cl	16.6	—
	-CMe_2Cl	21.0	—
	-CH_2Cl	16.1	3.0
	-CCl_3	13.9	0.24
$CHCl_2$-	-CH_2CH_3	124	6.3
	-CH_2Cl	74.2	0.78
	-$CHCl_2$	56.5	0.43

Logarithms of the relative reactivities for the methyl C–H bond are plotted against Taft's constants σ^* of the substituents in Fig. 1.

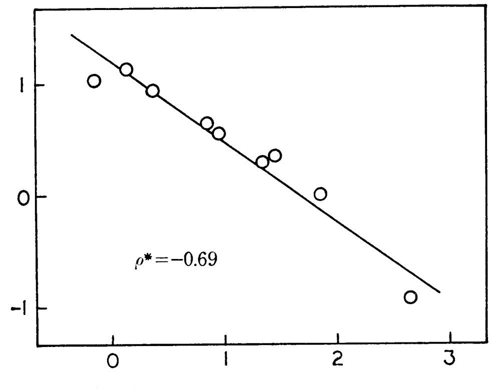
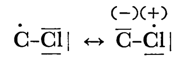


Fig. 1. Hammett plot for CH_3-*X*.

Good linear relationship was found to exist. The ρ^* value is -0.69, which is less negative than the value (-0.85) for chlorine atom reactions.[8] A similar trend of ρ values has been observed in the case of abstraction of benzylic hydrogen.[5,6] This indicates that *t*-butoxy radical is less electron-seeking than a chlorine atom.

Striking contrast to the chlorination with chlorine was observed in α-chlorine substituent effect. As was described previously,[11] a chlorine substituent will affect the reactivity of α-C–H bond in two ways. Its $-I$ effect will deactivate the α-C–H bond. Contrarily the conjugative effect will accelerate the hydrogen abstraction from the C–H bond, since the stabilization of the incipient radical by the following resonance will diminish the dissociation energy of the C–H bond being reacted:



$$\dot{C}\text{-}\overline{\underline{Cl}}| \leftrightarrow \overset{(-)}{\overline{C}}\text{-}\overset{(+)}{\dot{\underline{Cl}}}|$$

In photochlorination with chlorine, the following order of reactivities of C–H bonds were observed:

H-CH_2CH_2Cl>H-$CHClCH_2Cl$>H-CCl_2CH_2Cl
H-CH_2CCl_3>H-$CHClCCl_3$<H-CCl_2CCl_3

This indicates that the accelerating conjugative effect of α-chlorine substituent becomes more important than its inductive effect only when a strongly electron-withdrawing substituent like an trichloromethyl group is present in a substrate molecule.[11]

On the other hand, the present results for *t*-butyl hypochlorite chlorination show that an α-chlorine substituent always enhances the rate of hydrogen abstraction on this position. For example,

H-$CHClCH_2Cl$<H-CCl_2CH_2Cl
H-CH_2CCl_3<H-$CHClCCl_3$
H-$CH_2CH_2CH_2Cl$<H-$CHClCH_2CH_2Cl$

This tendency indicates that electron-donating conjugative effect of a substituent is quite an important factor controlling the rate of hydrogen abstraction by a *t*-butoxy radical. It has been pointed out that concerning the radicals X which form the bond (X–H) of essentially equal bond energy, hydrogen abstraction from the side chains of toluenes by the less electron-seeking radical X· showed a less negative value of ρ and a greater isotope effect (k_H/k_D).[12] Thus compared with the reaction

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[11] T. Migita, M. Kosugi and Y. Nagai, This Bulletin, **40**, 908 (1967).

[12] H. Sakurai and K. Tokumaru, "Chemistry of Free Radicals," Nankōdō, Tokyo (1967), Chap. 17, p. 355.

TABLE 4. COMPETITIVE EXPERIMENTS AT 40°C

Molar ratio of substrates	Molar ratio of products	Relative reactivities*	v.p.c. column
$CH_3CH_2CMe_3$	$CH_2ClCH_2CMe_3$	CH_3-CH_2CMe_3	Apiezon L
t-BuCl	CH_2ClCMe_2Cl		2.5 m
0.598	0.54	2.73	102°C
0.598	0.38	1.92	
0.598	0.59	2.98	
$CH_3(CH_2)_2CH_2Cl$	$CH_2Cl(CH_2)_2CH_2Cl$	CH_3-$CH_2CH_2CH_2Cl$	P.E.G. 6000
CH_2ClCH_2Cl	$CHCl_2CH_2Cl$		1.5 m
1.01	0.60	0.78	100°C
1.01	0.61	0.80	
1.01	0.61	0.80	
$CH_3CH_2CH_2Cl$	$CH_2ClCH_2CH_2Cl$	CH_3-CH_2CH_2Cl	P.E.G. 6000
CH_2ClCH_2Cl	$CHCl_2CH_2Cl$		1.5 m
1.31	0.59	0.60	100°C
1.31	0.51	0.52	
1.31	0.56	0.57	
t-BuCl	CH_2ClCMe_2Cl	CH_3-CMe_2Cl	D.O.P
CH_2ClCH_2Cl	$CHCl_2CH_2Cl$		2 m
1.07	0.21	0.27	78°C
1.07	0.21	0.26	
1.07	0.27	0.26	
$CH_3CHClCH_3$	$CH_2ClCHClCH_3$	CH_3-$CHClCH_3$	Apiezon L
t-BuCl	CH_2ClCMe_2Cl		2.5 m
1.20	0.85	0.85	76°C
1.20	0.88	0.88	
$CH_3CMeClCH_2Cl$	$CH_2ClCMeClCH_2Cl$	CH_3-$CMeClCH_2Cl$	D.E.G.S.
CH_2ClCH_2Cl	$CHCl_2CH_2Cl$		2.3 m
1.20	0.12	0.13	56°C
1.20	0.11	0.12	
$CH_3CHClCH_2Cl$	$CH_2ClCHClCH_2Cl$	CH_3-$CHClCH_2Cl$	P.E.G. 6000
$CH_2Cl(CH_2)_2CH_2Cl$	$CHCl_2(CH_2)_2CH_2Cl$		1.5 m
2.26	0.15	0.086	105°C
2.26	0.14	0.082	
CH_3CMeCl_2	$CH_2ClCMeCl_2$	CH_3-$CMeCl_2$	Apiezon L
CH_2ClCH_2Cl	$CHCl_2CH_2Cl$		2.5 m
1.75	0.082	0.062	100°C
1.75	0.080	0.061	
1.75	0.082	0.062	
CH_3CCl_3	CH_2ClCCl_3	CH_3-CCl_3	D.O.S.
CH_3CMeCl_2	$CH_2ClCMeCl_2$		2 m
1.99	0.12	0.12	100°C
1.99	0.14	0.13	
1.99	0.12	0.12	
$CH_2Cl(CH_2)_2CH_3$	$CHCl_2(CH_2)_2CH_3$	CH_2Cl-$(CH_2)_2CH_3$	P.E.G. 6000
CH_2ClCH_2Cl	$CHCl_2CH_2Cl$		1.5 m
1.01	1.35	2.63	100°C
1.01	1.36	2.70	
1.01	1.36	2.70	

TABLE 4. (Continued)

Molar ratio of substrates	Molar ratio of products	Relative reactivities*	v.p.c. column
$\underline{\mathrm{CH_2ClCH_2CH_3}}$	$\underline{\mathrm{CHCl_2CH_2CH_3}}$	$\underline{\mathrm{CH_2Cl}}\text{-}\mathrm{CH_2CH_3}$	P.E.G. 6000
$\mathrm{CH_2ClCH_2Cl}$	$\mathrm{CHCl_2CH_2Cl}$		1.5 m
1.31	1.38	2.09	100°C
1.31	1.21	1.81	
1.31	1.31	1.99	
$\underline{\mathrm{CH_2Cl(CH_2)_2CH_2Cl}}$	$\underline{\mathrm{CHCl_2(CH_2)_2CH_2Cl}}$	$\underline{\mathrm{CH_2Cl}}\text{-}\mathrm{(CH_2)_2CH_2Cl}$	P.E.G. 6000
$\mathrm{CH_2ClCH_2Cl}$	$\mathrm{CHCl_2CH_2Cl}$		1.5 m
1.11	1.93	1.74	104°C
1.11	1.82	1.64	
1.11	1.89	1.70	
$\underline{\mathrm{CH_2ClCMe_2Cl}}$	$\underline{\mathrm{CHCl_2CMe_2Cl}}$	$\underline{\mathrm{CH_2Cl}}\text{-}\mathrm{CMe_2Cl}$	D.E.G.S.
$\mathrm{CH_2ClCH_2Cl}$	$\mathrm{CHCl_2CH_2Cl}$		2.3 m
1.20	0.90	1.3	56°C
1.20	0.90	1.3	
$\underline{\mathrm{CH_2ClCCl_3}}$	$\underline{\mathrm{CHCl_2CCl_3}}$	$\underline{\mathrm{CH_2Cl}}\text{-}\mathrm{CCl_3}$	K.F. 96
$\mathrm{CH_2ClCH_2Cl}$	$\mathrm{CHCl_2CH_2Cl}$		3 m
2.76	1.21	0.88	108°C
2.76	1.16	0.84	
$\underline{\mathrm{CHCl_2CH_2CH_3}}$	$\underline{\mathrm{CCl_3CH_2CH_3}}$	$\underline{\mathrm{CHCl_2}}\text{-Et}$	X.F. 1105
$\mathrm{CH_2ClCH_2Cl}$	$\mathrm{CHCl_2CH_2Cl}$		2.0 m
1.53	2.92	7.65	64°C
$\underline{\mathrm{CHCl_2CHCl_2}}$	$\underline{\mathrm{CCl_3CHCl_2}}$	$\underline{\mathrm{CHCl_2}}\text{-}\mathrm{CHCl_2}$	Apiezon L
$\mathrm{CH_2ClCH_2Cl}$	$\mathrm{CHCl_2CH_2Cl}$		2.5 m
0.967	1.55	3.2	80°C
0.967	1.64	3.4	
0.967	1.74	3.5	
$\underline{\mathrm{CHCl_2CH_2Cl}}$	$\underline{\mathrm{CCl_3CH_2Cl}}$	$\underline{\mathrm{CHCl_2}}\text{-}\mathrm{CH_2Cl}$	Apiezon L
t-BuCl	$\mathrm{CH_2ClCMe_2Cl}$		2.5 m
0.483	0.97	18.0	80°C
0.483	0.97	18.3	
0.483	0.87	18.3	

Intramolecular reactivity pattern was found to be:

$\mathrm{CH_2Cl\text{-}CH_2\text{-}CH_2Cl}$
1.79 1.00

Competitive chlorination with 1,4-dichlorobutane was carried out to find relative reactivity of 2-position of 1,3-dichloropropane.

Molar ratio of substrates	Molar ratio of products	Relative reactivities*	v.p.c. column
$\underline{\mathrm{CH_2(CH_2Cl)_2}}$	$\underline{\mathrm{CHCl(CH_2Cl)_2}}$	$\underline{\mathrm{CH_2}}\!\left\langle\begin{smallmatrix}\mathrm{CH_2Cl}\\ \mathrm{CH_2Cl}\end{smallmatrix}\right.$	P.E.G. 6000
$\mathrm{CH_2Cl(CH_2)_2CH_2Cl}$	$\mathrm{CHCl_2(CH_2)_2CH_2Cl}$		1.5 m
2.13	0.38	0.35	104°C
2.13	0.36	0.34	
2.13	0.34	0.33	

* Relative to that of a C–H bond of the other substrate.

of a chlorine atom, hydrogen abstraction by the less electron-seeking *t*-butoxy radical would be influenced by a polar factor in a less extent (less ρ^* value), and by bond dissociation energy of substrate C–H in a greater extent. The tendencies are in agreement with this generalization.

Experimental

Materials. *t*-Butyl hypochlorite and di-*t*-butyl peroxide were prepared by the method of Teeter and Bell,[13]

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[13] H. M. Teeter and E. W. Bell, "Org. Syn"., Vol. 32, 20 (1952).

and Milas and Surgenor,[14] respectively. Dichloromethane, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, pentachloroethane, neohexane, propylene chloride, 1,3-dichloropropane and 1,4-dichlorobutane were purified by fractionating commercial materials, and their purities were checked by means of v.p.c.

t-Butyl chloride, 2,2-dichloropropane and *n*-propyl chloride were prepared by the method previously described.[8,11] *n*-Butyl chloride and isopropyl chloride were prepared by a method analogous to the synthesis of *n*-propyl chloride.[15] 1,2-Dichloro-2-methylpropane was obtained by the chlorination of *t*-butyl chloride, bp 106°C[16] Among the authentic samples of chlorination products, 1,2,2-trichloropropane and 1-chloro-3,3-dimethylbutane have been identified previously.[8,11] 1,1,2-Trichloro-2-methylpropane and 1,2,3-trichloro-2-methylpropane were collected by v.p.c. from the reaction mixtures of chlorination of 1,2-dichloro-2-methylpropane by *t*-butyl hypochlorite, and identified on the basis of their NMR spectrum. (τ values).

$(CH_3{}^1)_2CClCH^2Cl_2$ 8.21 (H^1 singlet)
4.23 (H^2 singlet)

$CH_3{}^1CCl(CH_2{}^2Cl)_2$ 8.28 (H^1 singlet)
6.22 (H^2 singlet)

1,2,3-Trichloropropane was prepared by adding a chlorine to allyl chloride, bp 155—158°C.[17] 1,1-Dichlorobutane was prepared by treating *n*-butyraldehyde with phosphorus pentachloride, bp 114°C.[18] 1,1,4-Trichlorobutane was collected by v.p.c. from the chlorination mixture of 1,4-dichlorobutane and identified with its NMR spectrum (τ values).

$CH^1Cl_2\text{-}CH_2{}^2\text{-}CH_2{}^3\text{-}CH_2{}^4Cl$ 4.17 (H^1 triplet)
7.3—8.2 (H^2, H^3 multiplet) 6.41 (H^4 triplet)

$(CH_3{}^1)_2COHCH_2{}^2Cl$ 8.74 (H^1 singlet)
6.56 (H^2 singlet)

1-Chloro-2-methyl-2-propanol was collected by v.p.c. from the reaction mixture of chlorination of 2,2-dichloropropane by *t*-butyl hypochlorite, and identified by comparing its NMR spectrum and v.p.c. retention time (X.F. 1105, P.E.G. 6000 and D.O.S. column) with that of an authentic sample (τ values).[19]

Determination of the Ratio of Chloride and *t*-Butyl Alcohol. A mixture of chloride and *t*-butyl hypochlorite (*ca.* 10: 1 molar ratios) was placed in a reaction tube. After the mixture was degassed in a dark place, the tube was sealed and immersed in a thermostat (40°C ±0.1) and irradiated with 500 W tungsten lamp until the color of chlorine in the mixture disappeared. Analysis of the products was carried out by v.p.c. method employing 1.5 m column of P.E.G. 6000.

Determination of Relative Reactivities. Reactions were carried out in sealed, degassed tubes as described above. For the decomposition of di-*t*-butyl peroxide, pyrex tubes were used and irradiated for 24 hr with 300 W high pressure mercury lamp. Analysis of the acetone and the *t*-butyl alcohol was carried out by v.p.c. method employing 2.0 m column of D.O.P. Relative values of k_a/k_d were calculated by the amounts of acetone and *t*-butyl alcohol.[10] Average values of three runs are presented in Table 2.

Competitive reactions were carried out with mixtures of two chloroalkanes and *t*-butyl hypochlorite (*ca.* 10: 1 molar ratios). Relative reactivities were calculated by the ratio of the chlorination products and the substrates. Analysis of the chlorination products was carried out by v.p.c. Table 4 shows the results. From these values, reactivities of C–H bonds of chloroalkanes relative to that of 2,2-dichloropropane were calculated as shown in Table 3.

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17) M. S. Kharasch and H. C. Brown, *J. Amer. Chem. Soc.*, **61**, 2142 (1939).

18) H. C. Brown and A. B. Ash, *ibid.*, **77**, 4019 (1955).

19) The sample was supplied by Dr. S. Sekiguchi[20] of this university.

20) S. Sekiguchi, H. Inoue, M. Hayashi and K. Matsui, *Kagyo Kagaku Zasshi*, **71**, 1943 (1968).