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Positive Halogen Compounds. II. Radical Chlorination of Substituted Hydrocarbons with *t*-Butyl Hypochlorite[1]

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Relative reactivities in competitive chlorination and isomer distributions observed with 1-chlorobutane, butyronitrile, *n*-propyl acetate and similar compounds indicate a strong polar effect in chlorinations carried out with *t*-butyl hypochlorite. Competitive chlorinations of substituted toluenes give a Hammett ρ-value of -0.83 and it is concluded that the polar properties of the *t*-butoxy radical are very similar to that of the chlorine atom. However, C–H bond dissociation energies appear to be more important in determining the point of *t*-butoxy radical attack than is the case with chlorine atoms.

Evidence was presented in our previous paper[2] that *t*-butyl hypochlorite chlorinates saturated hydrocarbons by a radical chain process involving as major chain-propagating steps the sequence

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \qquad (1)$$

$$R\cdot + (CH_3)_3COCl \longrightarrow RCl + (CH_3)_3CO\cdot \qquad (2)$$

In this scheme, relative reactivities of hydrocarbons and distributions of chlorinated isomers are determined by the relative reactivities of different types of C–H bond toward the chain-carrying *t*-butoxy radical, and results of competitive measurements with a variety of aliphatic and alkyl aryl hydrocarbons were described. In this paper, the study has been extended to substituted hydrocarbons, with results which provide a better picture of the scope of *t*-butyl hypochlorite as a practical chlorinating agent, and also of the role of polar effects in the reaction of the *t*-butoxy radical.

Results and Discussion

Relative Reactivities of Substituted Toluenes.—Perhaps the most reliable way of isolating electronic effects upon rates and equilibria in organic reactions is by investigating the effect of *m*- and *p*-substituents upon the side chain reactions of benzene. Although originally developed in the study of heterolytic (ionic) reactions, it has also proved useful in assessing the magnitude of polar effects in free radical processes.[3] Results of a series of competitive chlorinations of substituted toluenes by *t*-butyl hypochlorite at 40° are given in Table I (data for xylenes are taken from our previous paper).

TABLE I

RELATIVE REACTIVITIES OF TOLUENES TOWARD *t*-BUTYL HYPOCHLORITE AT 40°

Substituent	Relative reactivity
p-CH_3	1.53 ± 0.05[a]
m-CH_3	1.17 ± .03[a]
None	1.00
p-Cl	0.71 ± .01
m-Cl	0.52 ± .02

[a] Experimental result divided by statistical factor of 2.

In Fig. 1, the data are plotted against Hammett σ-values[4] for the substituents, and also against the σ^+-values of Brown and Okamoto[5] for the *p*-substituents. Two observations are evident from Fig. 1. The plot against σ-values gives a reasonably good linear relation corresponding to a Hammett ρ-value of -0.83 for reaction 1. This may be compared with the values for chlorine[6] and bromine[7] atom reactions with toluene (-0.76 and -1.05, respectively) and implies that the *t*-butoxy radical is an electron-accepting species preferentially attacking points of high electron availability, with polar properties quite similar to the chlorine atom. Second, the correlation with σ-values of substituents is rather better than with σ^+-values. This again parallels the chlorine atom reaction, and, as pointed out by Russell,[8] is consistent with a strongly exothermic low activation energy process, in which, from Hammond's postulate,[9] there is little bond-breaking in the transition state.

Relative Reactivities and Isomer Distributions in other Substituted Hydrocarbons.—Results of relative reactivity determinations for a number of substituted hydrocarbons relative to toluene and cyclohexane are given in Table II, while Table III gives distributions of chlorinated isomers obtained from molecules containing more than one type of C–H bond. From Table II it is again evident that, qualitatively, electron-withdrawing groups decrease reactivity. Thus, reactivity per benzyl C–H in benzyl chloride is only 0.72 that per C–H in toluene, and all of the aliphatic derivatives are less reactive than cyclohexane, both per molecule and, more significantly, per secondary C–H bond. Paralleling this observation we see (Table III) that electron-withdrawing groups preferentially deactivate nearby C–H bonds, leading to increased substitution at more remote points in the molecule.

TABLE II

RELATIVE REACTIVITIES OF SUBSTITUTED HYDROCARBONS (40°)

Cyclohexane	6.00 ± 0.09[a]
Cyclopentanone	1.53
n-Butyl chloride	1.48 ± 0.04
Toluene	1.00
n-Propyl acetate	0.64 ± 0.02
Benzyl chloride	.48
Butyronitrile	.18

[a] Experimental errors when given represent spread of duplicate experiments; other figures are single experiments.

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[1] Taken from the Ph.D. Dissertation of B. B. Jacknow, 1960. Partial support by the Office of Ordnance Research, U.S. Army, is gratefully acknowledged.

[2] C. Walling and B. B. Jacknow, THIS JOURNAL, **82**, 6108 (1960).

[3] For general discussion, *cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 132 ff.

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

[5] H. C. Brown and Y. Okamoto, THIS JOURNAL, **79**, 1913 (1957).

[6] C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957).

[7] E. C. Kooyman, R. van Helden and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschappen Proc.*, **B56**, 75 (1953).

[8] G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

[9] G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

TABLE III

ISOMER DISTRIBUTIONS IN *t*-BUTYL HYPOCHLORITE CHLORINATION OF SUBSTITUTED HYDROCARBONS (40°)[a]

	Indicated isomer, %			
	1,1	1,2	1,3	1,4
1-Chlorobutane	21.0 ± 0.4	19.4 ± 0.1	43.9 ± 0.3	15.6 ± 0.1
(4 *M* CCl_4)	21.3 ± .2	19.6 ± .1	43.6 ± .1	15.4 ± .2
(4 *M* C_6H_6)	21.4 ± .1	19.0 ± .1	46.4 ± .1	13.2 ± .1
(4 *M* *t*-$C_4H_9C_6H_5$)	23.6 ± .3	17.3 ± .1	49.0 ± .2	10.1 ± .2
1,1-Dichlorobutane	30.6 ± .3	8.1 ± .1	38.8 ± .2	22.5 ± .1
1-Chloropropane	47.7	41.4	10.9	....
n-Propyl acetate	29.3 ± .2	43.0 ± .5	25.4 ± .4	(2.3 ± .1)[b]
1-Nitropropane	12.5 ± .1	33.4 ± .5	54.0 ± .5	....
Butyronitrile	22.4 ± .3	43.7 ± 2.5	39.9 ± 2.2	

[a] Experimental errors, when given, represent spread of duplicate experiments, or ±0.1% when agreement was better. Other figures are single experiments. Solvents, when employed, are given in parentheses. [b] % substitution on CH_3COO-.

These observations can be put in more quantitative form by combining the results of Tables II and III and calculating relative reactivities per C–H bond for those molecules for which both pieces of data are available. Here it is convenient to choose as standard the primary C–H bond of 2,3-dimethylbutane (relative reactivity *vs.* toluene C–H 0.095[2]). Results of this comparison appear in Table IV. Since the reactivity of secondary C–H bonds of unsubstituted hydrocarbons range from 8–16 on this scale[10] the deactivation of C_1–H and C_2–H bonds is unmistakable. By the time carbon 3 is reached reactivities appear to be in the normal range for secondary (1-chlorobutane) or primary (the other examples) C–H bonds.

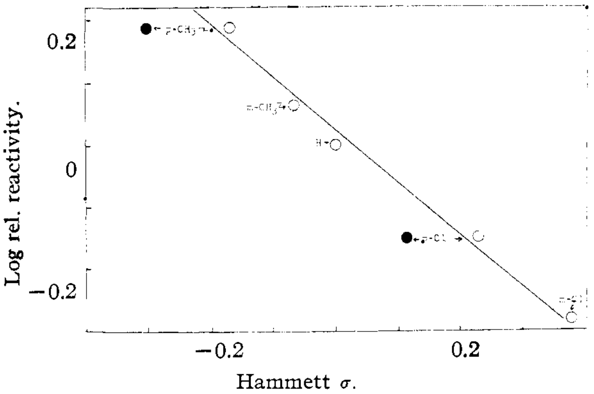

Fig. 1.—Relative reactivities of substituted toluenes toward *t*-butyl hypochlorite *vs.* Hammett σ-values for substituents. Filled circles represent σ^+-values for *p*-substituents.

If these results are to be compared with chlorine atom reactions, it must be kept in mind that they must arise from the interaction of two factors: overall energetics, determined by the strength of C–H bonds broken and the resonance stabilization of the resulting radical, and the polar properties of the *t*-butoxy radical. As shown in our previous paper,[2] *t*-butoxy radical reactions are considerably more sensitive to bond strength than are chlorine atom processes (*p*:*s*:*t* ratios being approximately 1:8:44 compared to 1:3:4.5). On the other hand, our results on substituted toluenes above indicate that the polar properties of the two radicals are about equal. This comparison appears to account quite well for the differences between our isomer distributions in Table III, and those reported for chlorine atom chlorination, Table V. In general, and particularly in the cases of 1,1-dichlorobutane and butyronitrile, the weakest C–H bond in each molecule is that on C_1, and *t*-butyl hypochlorite gives significantly more substitution at this point.

TABLE IV

RELATIVE REACTIVITIES OF C–H BONDS IN *t*-BUTYL HYPOCHLORITE CHLORINATION *vs.* PRIMARY C–H (2,3-DIMETHYLBUTANE)

Compound	Relative reactivity C_1–H	C_2–H	C_3–H	C_4–H
1-Chlorobutane	5.1	4.6	10.2	2.4
n-Propyl acetate	3.0	4.4	1.7	(0.52)[a]
Butyronitrile	0.67	1.3	0.67	...

[a] Acetoxy C–H.

TABLE V

COMPARISON OF ISOMER DISTRIBUTIONS IN Cl_2 AND *t*-C_4H_9OCl CHLORINATIONS

Molecule	Reagent	Isomer distribution, % 1,1	1,2	1,3	1,4
1-Chlorobutane	C_4H_9OCl	21.1	19.4	43.9	15.6
	Cl_2[11]	7.8	23.5	49.2	19.5
1,1-Dichlorobutane	C_4H_9OCl	30.6	8.1	38.8	22.5
	SO_2Cl_2 (70°)[12]	2	12	49	37
1-Chloropropane	C_4H_9OCl	47.7	41.4	10.9	
	SO_2Cl_2 (70°)[12]	0	60	40	
n-Propyl acetate	C_4H_9OCl	29.3	43.0	25.4	(2.3)[a]
	Cl_2[13]	25	30	49	(0)[a]
Butyronitrile	C_4H_9OCl	22.4	43.7	33.9	
	Cl_2[14]	0	69	31	

[a] Substitution on CH_3COO-.

Only with *n*-propyl acetate do we observe some attack as well on the relatively weak H–CH_2COO– bond[15] by hypochlorite.

Finally, Table III contains results on some experiments on the effect of solvents on the isomer distribution obtained from the *t*-butyl hypochlorite chlorination of 1-chlorobutane. As in the case of *t*-butyl hypochlorite chlorination of hydrocarbons[2]

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(10) The *s*/*p* ratio for *n*-butane is approximately 8 (see ref. 2); on the other hand, direct comparison of cyclohexane and 2,3-dimethylbutane gives *s*/*p* = 15.9.

(11) C. Walling and M. F. Mayahi, THIS JOURNAL, **81**, 1485 (1959).

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

(13) A. Bruylants, M. Tits and R. Danby, *Bull. soc. chim. Belges*, **58**, 210 (1949).

(14) A. Bruylants, M. Tits, C. Dieu and R. Gauthier, *ibid.*, **61**, 266 (1952).

(15) No direct measurements of the effect of acetoxy or carbonyl groups on C–H bond strengths are available. However, one of us has recently estimated (admittedly rather empirically) that the resonance stabilization of the resulting radicals amounts to 4 and 25 kcal., respectively; C. Walling, *J. Phys. Chem.*, **64**, 166 (1960).

a small solvent effect is observed, with a sharpening of the distribution in aromatic solvents, much as is found in the chlorine atom reaction.

Experimental

Materials were in general commercial materials, purified by distillation as required, and their purity checked by physical constants and gas chromatography. The *t*-butyl hypochlorite was prepared as described previously.[2]

Competitive reactions were run on small samples in sealed, degassed tubes using photochemical initiation and analyzed for unreacted substrates by gas chromatography using internal standards (usually CCl_4 or chlorobenzene) as in previous work.[2] Relative reactivities were calculated by the usual relation $\log (A/A_0)/\log (B/B_0) = r$ where r represents the ratio of rate constants for *t*-butoxy radical attack on substrates B and A.

Isomer distributions were determined by gas chromatographic analysis of reaction products obtained from approximately 10:1 ratios of substrate and *t*-butyl hypochlorite to minimize poly-chlorination. Isomer yields were considered proportional to peak areas, and peaks were definitely identified by product isolation (either by gas chromatography of fractional distillation of larger runs) and the determination of physical constants.

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Resonance Interactions of Substituents Attached to the Same Saturated Carbon Atom. Reactivity of Polychloromethyl Ethers[1]

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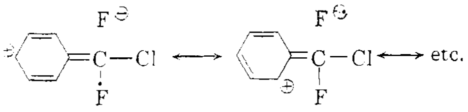
Solvolysis rates were determined for *p*-methoxybenzyl chloride, *p*-methoxybenzal chloride, methyl chloromethyl ether, methyl dichloromethyl ether and methyl trichloromethyl ether. All of the solvolyses are believed to proceed by the SN1 mechanism. It was found that α-chloro substituents increase the reactivity of the benzyl chlorides but decrease that of the chloromethyl ethers. This is attributed to the greater stabilization of the reactants by additional contributing structures of the type $CH_3O^+{=}CHCl\ Cl^-$ than stabilization of the transition state leading to the carbonium ion by contributions of additional structures in which the positive charge is placed on the α-chlorine.

Introduction

In a study of the effect of α-halogen substituents on SN1 reactivity, using benzyl halides and their derivatives, it was found that (compared to α-hydrogen) α-bromine atoms strongly increased the rate of carbonium-ion formation and α-chlorines had an even greater activating effect. The activating influence of α-fluorine was found to be much smaller than either bromine or chlorine and, in fact, it is not even certain that the α-fluorine (compared to α-hydrogen) activates at all.[2,3] A linear free energy correlation of the rates of basic hydrolysis of haloforms, however, gave strong evidence that in the decomposition of trihalomethyl anions, a process that can also be viewed as an SN1 reaction, α-fluorine powerfully increased the reaction rate compared to α-chlorine and bromine substituents.[5] It was suggested that in both cases the greater electronegativity of fluorine tended to decrease the SN1 reactivity while the greater ability of fluorine to donate its unshared electron pairs tended to increase the SN1 reactivity. In the case of the trihalomethyl anions the latter effect was stronger, but in the case of the benzyl halides the electronegativity effect was more important because of its manifestation in the form of the contribution of structures of the type



which have no counterpart in the trihalomethyl anion and whose analogs could not contribute significantly to the total structure of the carbonium ion formed by ionization of the chloride ion. Such resonance stabilization, resulting from the presence of a group with a highly electron-withdrawing inductive effect on the same carbon with a group capable of electron donation by a resonance effect, has been recognized by Brockway, for example, to cause unusually short bond distances in the polyfluoromethanes[6] and is probably at least partly responsible for the great unreactivity of organic polyfluorides. More direct evidence may be found in Petersen and Pitzer's observation of the strong tendency of difluorodichloromethane to disproportionate[7] and the fact that heats of formation show that the disproportionation of methylene fluoride[8] to carbon tetrafluoride[9] and methane[10] should be exothermic by about 12 kcal. per mole. Since chlorine is both less electronegative and less capable of electron donation by a resonance effect, it is not surprising that this effect, while probably still present, is much smaller with the poly*chlorides* of methane. However, if the chlorine were on a carbon atom to which a considerably more strongly resonance-electron-donating group were attached,

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[1] Part IX in the series, "The Effect of Halogen Atoms on the Reactivity of Other Halogen Atoms in the Same Molecule." For part VIII see J. Hine and R. G. Ghirardelli, *J. Org. Chem.*, **23**, 1550 (1958). Abstracted from the Ph.D. thesis of Robert J. Rosscup, Georgia Institute of Technology, 1960.

[2] J. Hine and D. E. Lee, THIS JOURNAL, **73**, 22 (1951); **74**, 3182 (1952).

[3] This uncertainty is due to the fact that in 50% aqueous acetone benzyl bromide and benzyl chloride themselves are believed to react by an SN2 mechanism to a considerable extent.[4] The solvolysis rates for these compounds can thus be regarded only as maximum values for the SN1 reactivity and we have not used data on these compounds in any of the quantitative arguments given in this article.

[4] *Cf.* C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 329.

[5] J. Hine and S. J. Ehrenson, THIS JOURNAL, **80**, 824 (1958).

[6] L. O. Brockway, *J. Phys. Chem.*, **41**, 185, 747 (1937).

[7] D. E. Petersen and K. S. Pitzer, *ibid.*, **61**, 1252 (1957).

[8] C. A. Neugebauer and J. L. Margrave, *ibid.*, **62**, 1043 (1958).

[9] C. A. Neugebauer and J. L. Margrave, *ibid.*, **60**, 1318 (1956).

[10] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, p. 466.