[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Rates of Solvolysis of the Halophenyldimethylcarbinyl Chlorides. The Effect of Halogen Substituents upon the Rates of Electrophilic Reactions[1-3]

BY HERBERT C. BROWN, Y. OKAMOTO AND GEORGE HAM

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The twelve *o*-, *m*- and *p*-monohalophenyldimethylcarbinyl chlorides were synthesized and their rates of solvolysis in 90% aqueous acetone (by volume) determined at several temperatures. Within each of the three isomeric series, the observed order of reactivity is F > Cl > Br < I. The observed magnitudes of the rate constants together with the observed reactivity orders can be rationalized in terms of the inductive effect, resonance and steric inhibition of resonance. Thus in the *meta* series it appears that the inductive effect is dominant, with a minor resonance contribution which increases the electron density at the *ortho* positions, whence it is relayed to the electron deficient reaction center by induction. In the *para* position, both induction and resonance appear to be of nearly equal (but opposite) effect. The lower rates exhibited by the *ortho* halogen substituents are attributed to an increased inductive effect and a reduced resonance effect, the latter arising from a partial resonance inhibition due to the conflicting steric requirements of the *ortho* substituents and the coplanar dimethylcarbinyl group of the incipient carbonium ions.

The quantitative understanding of the chemical effects of halogen substituents has long provided a difficult hurdle for organic theory.[4,5] From the relative electronegativity of the halogens,[6] it would be anticipated that the electron-withdrawing effect of these substituents would decrease with increasing atomic weight, F > Cl > Br > I. However, this order is rarely observed. It is apparently exhibited by the monohaloacetic acids[5] and by the 2-halopyridines[7] but is conspicuous by its absence in other systems for which data are available.

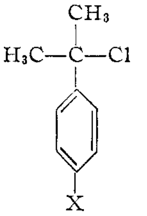
The difficulty is attributed to the resonance possibilities in the halogen substituents. Such resonance will serve to reduce the electron-withdrawing tendencies of the halogens. It was pointed out by Dippy and Lewis that any order, from F > Cl > Br > I, to the opposite order, F < Cl < Br < I could be realized by a judicious combination of these two opposing effects.[8]

In order to attain a better understanding of the behavior of these substituents, it appeared desirable to examine their influence in a reaction which was strongly electron demanding. In view of the insight into the behavior of alkyl groups provided by our study of the solvolysis of the alkylphenyldimethylcarbinyl chlorides,[9] we decided to undertake a similar study of the halophenyldimethylcarbinyl chlorides, X = F, Cl, Br, I (I–III).

Results

The various halobenzoic acids were converted into the methyl or ethyl esters and treated with methylmagnesium iodide to form the halophenyldimethylcarbinols. Physical properties and analytical data for these carbinols are summarized in Table I.

The tertiary carbinols were treated with dry hydrogen chloride to form the tertiary chlorides. The rates of solvolysis of these chlorides were determined in 90% aqueous acetone (by volume) at three temperatures. The rate constants and derived data are summarized in Table II.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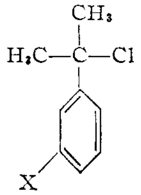
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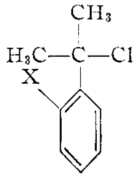
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In this series of closely related compounds the log *A* (or entropy) terms do not exhibit major variations and the energy of activation (or enthalpy) terms parallel the reaction rates closely. Theoretically, it would be preferable to consider structural changes from their effect upon the energy terms (E_{act} or $\Delta H\ddagger$). However, these derived terms are subject to much greater uncertainty than the experimentally determined rate constants. Consequently, the following discussion will be based upon these quantities at 25°. Since the log *A* (or entropy) terms do not exhibit any important variations, the rate constants and the energy terms should be simply related and no difficulty should be introduced as a result of this procedure.

Discussion

The *meta* position in aromatic systems should be relatively insensitive to resonance or steric effects and, consequently, should be the most favorable position for observations on the importance of the inductive effect. An alkyl group in the *meta* position of phenyldimethylcarbinyl chloride increases the rate of solvolysis by a factor of 2.[9] This increase is in accord with the postulated +I effect of alkyl groups and the electron deficient character of the transition state in the solvolysis reaction.

Halogen substituents in the *meta* position have the opposite effect. The rates of solvolysis are reduced over that of the parent compound by factors between 40 and 70 (Table II). This is in accord both with the postulated −I effect of halogen substituents[5] and their highly electronegative

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[1] Directive Effects in Aromatic Substitution. XII.

[2] Supported in part by the Petroleum Research Fund of the American Chemical Society.

[3] Based upon a thesis submitted by Y. Okamoto, in 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[4] M. L. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938); J. W. Baker and H. B. Hopkins, *ibid.*, 1089 (1949).

[5] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 733 ff.

[6] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

[7] H. C. Brown and D. H. McDaniel, THIS JOURNAL, **77**, 3752 (1955).

[8] J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 649 (1936).

[9] H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, THIS JOURNAL, **79**, 1897 (1957).

TABLE I

PHYSICAL PROPERTIES OF THE HALOPHENYLDIMETHYLCARBINOLS

Halogen substituent	Physical properties B.p. °C.	Mm.	M.p., °C.	$n^{20}D$	Analyses, % Calcd. C	H	Found C	H
o-Fluoro[a]	74.8	8	29–30		70.11	7.15	70.09	7.26
m-Fluoro	87	7		1.4995	70.11	7.15	69.94	7.36
p-Fluoro	86	8.2	37.8		70.11	7.15	70.17	7.31
o-Chloro[b]	79.2	2.2	23.7	1.5416	63.34	6.45	62.98	6.30
m-Chloro[a]	88.0	2.2		1.5370	63.34	6.45	63.29	6.29
p-Chloro	92.5	3	43.3		63.34	6.45	63.50	6.73
o-Bromo[a]	112	5.2		1.5634	50.25	5.12	50.23	5.11
m-Bromo	104.5	3.2		1.5602	50.25	5.12	50.28	5.32
p-Bromo			45.6		50.25	5.12	50.78	5.43
o-Iodo[a]	121	5.5		1.6017	41.24	4.23	41.04	4.22
m-Iodo			59–61		41.24	4.23	40.97	4.28
p-Iodo			57–57.5		41.24	4.23	41.33	4.21

[a] E. Bergmann and A. Weizmann, *Trans. Faraday Soc.*, **32**, 1318 (1936). [b] C. K. Bradsher and E. S. Smith, THIS JOURNAL, **65**, 1643 (1943).

TABLE II

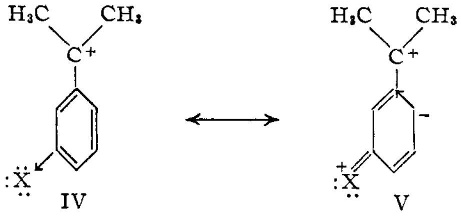
RATE CONSTANTS AND DERIVED DATA FOR THE SOLVOLYSIS OF THE HALOPHENYLDIMETHYLCARBINYL CHLORIDES IN 90% AQUEOUS ACETONE

Halogen substituent	Rate constants, k_1 (sec.$^{-1}$ × 10^5) 0°	15°	25°	35°	40°	45°	55°	Rate ratio (25°)	*E*act	log *A*	Δ*H*‡	Δ*S*‡
Hydrogen[a]	0.600		12.4	36.1				1.00	19.5	10.4	18.8	−12.5
o-Fluoro			0.622		3.44		15.8	0.0502	20.9	10.1	20.3	−14.4
o-Chloro			.0975		0.625		3.39	.00786	23.0	10.8	22.3	−11.1
o-Bromo			.0753		.517		2.67	.00606	23.1	10.8	22.5	−11.1
o-Iodo			.137		.839		4.56	.0110	22.7	10.8	22.1	−11.4
m-Fluoro			.311		1.65		7.39	.0251	20.5	9.5	19.9	−17.0
m-Chloro			.194		1.13		5.25	.0156	21.3	9.9	20.7—	−15.1
m-Bromo			.178		1.06		5.44	.0144	22.1	10.5	21.5	−12.7
m-Iodo			.289		1.59		7.22	.0233	20.8	9.7	20.2	−16.1
p-Fluoro	1.32	8.44	26.5					2.14	19.4	10.6	18.8	−11.7
p-Chloro	0.163		3.78		18.1			0.305	20.0	10.2	19.5	−13.6
p-Bromo			2.58	7.83		21.2		.208	19.9	10.0	19.2	−15.2
p-Iodo			3.03	9.00		24.0		.244	19.5	9.8	18.8	−16.0

[a] Ref. 9.

character. However, the observed order of rates, F > Cl > Br < I, does not agree with that anticipated, F < Cl < Br < I, on the basis of the decrease in electronegativity with increasing atomic weight of the halogen.[6]

In order to account for the observed order of the *meta* alkyl substituents (Me > Et > *i*-Pr > *t*-Bu), it was necessary to postulate a small hyperconjugative component which increased the electron densities at the *ortho* positions of the aromatic ring, whence it could be relayed by induction to the electron deficient reaction center.[9] A similar explanation appears necessary in order to account for the observed order for the halogen substituents (IV, V).



IV V

It is generally recognized that the ability of the halogens to engage in resonance with double-bonded structures is greatest for fluorine and decreases with increasing size of the halogen.[10] Consequently, the observed effect of *meta* halogen substituents is in accord with a large electron-withdrawing inductive effect (IV), decreasing in the order, F > Cl > Br > I, accompanied by a considerably smaller electron-supplying resonance effect (V), the magnitude of which decreases in the same order, F > Cl > Br > I.

The relative order exhibited by the halogens in the *para* position, F > Cl > Br < I, is the same as that observed for the *meta* derivatives (Fig. 1). However, the effect of the halogen upon the rate is much less than for the *meta* compounds, chlorine, bromine and iodine reducing the rates by the relatively small factors of 3.3, 4.8 and 4.1, respectively. Moreover, instead of a reduction in rate, the *p*-fluoro derivative exhibits an enhanced rate, more than twice that of the unsubstituted parent compound.

No new factors need be called in to account for these observations. It is sufficient to postulate that in the *para* position, with the possibility for direct resonance interaction of the halogen substituent with the electron deficient reaction center (VII), the resonance and inductive components become of comparable magnitude. In the case of

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(10) A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949.

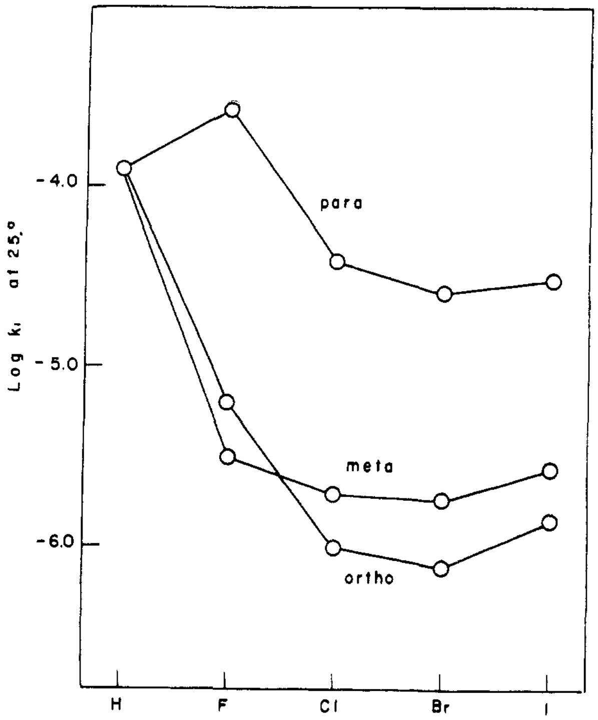
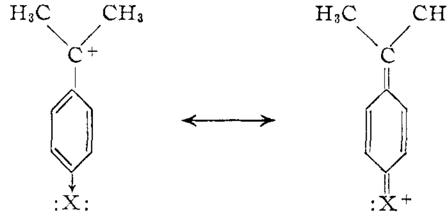


Fig. 1.—Effect of halo substituents upon the rates of solvolysis of the halophenyldimethylcarbinyl chlorides in 90% aqueous acetone at 25°.

chlorine, bromine and iodine, the inductive factors are slightly larger, so that a small net electron-withdrawing effect results and the observed rates are somewhat smaller than that of the parent compound. In the case of fluorine, the resonance effect is slightly larger than that of the inductive effect, resulting in a small net electron donation to the reaction center, with a small increase in rate over that of the unsubstituted derivative.

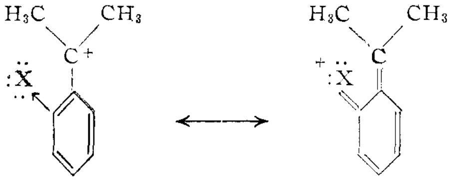


VI VII

The observed order for the *ortho* halo derivatives, F > Cl > Br < I, is the same as that previously noted for the *meta* and *para* compounds. However, the magnitude of the rate constants is considerably smaller than those of the *para* derivatives and resemble much more closely the values obtained with the *meta* compounds. Moreover, the ratios of the rates of the *ortho* and *para* substituents (k_0/k_p) exhibit a measure of constancy: fluoro, 0.024; chloro, 0.026; bromo, 0.029; iodo, 0.045.

A similar effect was observed previously in the corresponding alkyl derivatives[9]: k_0/k_p for methyl, 0.14; ethyl, 0.094; isopropyl, 0.045. In the case of these alkyl groups the decrease in rate of the *ortho* derivatives is reasonably ascribed to steric inhibition of resonance (hyperconjugation).[11] The decrease in the value of the k_0/k_p ratios with increasing steric requirements of the alkyl substituents is in agreement with this interpretation.

The van der Waals radii of chlorine and bromine are believed to be very similar to that of the methyl group.[6] Consequently, it is not unreasonable to attribute the major portion of the decrease observed in the solvolysis rates of the *o*-halophenyldimethylcarbinyl chlorides to steric inhibition of resonance (VIII, IX).



VIII IX

It is not possible to attribute the entire decrease to this factor alone. First, the ratios for chlorine and bromine are smaller than those observed for methyl, whereas the van der Waals radii for these groups are quite similar. Secondly, the ratios *increase* from fluorine to iodine, whereas a decrease in ratio would have been expected in view of the rise in steric requirements of the halogens. It is possible to account for the complete behavior of the *ortho* halogen substituents by including in the treatment an inductive effect which is relatively large compared with that in the *para* position.

On the one hand, it is gratifying that it is possible to account for the observed behavior of this series of compounds in terms of well-recognized concepts of current organic theory.[5] On the other hand, an essentially qualitative treatment of this kind for quantitative data cannot be considered highly satisfying. An analysis of the kind made possible by the Hammett equation[12,13] should provide a far more quantitative basis for treating structural effects. However, it has usually been considered that electrophilic reactions of the type here discussed cannot be handled in terms of the Hammett treatment. Our recent exploration of the quantitative treatment of aromatic substitution in terms of the Hammett equation utilizing modified substituent constants[14] encouraged us to examine the present data from that viewpoint. The results of this examination will be presented in a subsequent paper.[15]

Experimental Part

Halophenyldimethylcarbinols.—Commercially available halobenzoic acids were recrystallized to constant melting point (Table III). These were converted into the methyl or ethyl esters by standard esterification procedures in yields of approximately 90%. The esters were fractionated at low pressures. The observed physical properties are summarized in Table III.

The halophenylcarbinols were prepared by the following general procedure. In the usual 1-liter Grignard assembly 0.55 mole of methylmagnesium iodide in 200 ml. of ether was prepared. To this solution was added 0.25 mole of the ester in 150 ml. of ether. The reaction product was decom-

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(11) G. Baddeley, J. Chadwick and H. T. Taylor, *J. Chem. Soc.*, 448 (1956).

(12) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(13) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(14) C. W. McGary, Y. Okamoto and H. C. Brown, THIS JOURNAL, **77**, 3037 (1955).

(15) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).

TABLE III

PHYSICAL PROPERTIES OF INTERMEDIATES

Substituent	Benzoic acid M.p., °C.[a]	Methyl benzoate B.p. °C.	Methyl benzoate Mm.	Methyl benzoate n^{20}_D	Ethyl benzoate B.p. °C.	Ethyl benzoate Mm.	Ethyl benzoate n^{20}_D
o-Fluoro	128				85.5	8	1.4920
m-Fluoro	124.5				84	9.2	1.4848
p-Fluoro	183.5				87.5	11	1.4860
o-Chloro	141	99	8.5				
m-Chloro	154.5	106	13				
p-Chloro	240.5	112.5	8		65	1	1.5239
o-Bromo	150				135	15	1.5436
m-Bromo	154				131	17	1.5428
p-Bromo	255				129	15	1.5460
o-Iodo	163	103.5	1	1.6052			
m-Iodo	187				114	2.1	1.5830
p-Iodo	268				126.5	4	1.5877

[a] Melting point range 0.5–1.0°.

posed with saturated ammonium chloride solution and cracked ice. The ether layer and ether extracts were combined, dried with anhydrous potassium carbonate and the ether removed on a steam-cone. The product was carefully distilled at low pressures (usually 2–5 mm.) through a small fractionating column fitted with a glass spiral core. Yields of approximately 70–75% were realized. The physical properties and analyses are summarized in Table I.

Halophenyldimethylcarbinyl Chlorides.—A weighed 30-ml. round bottom flask equipped with a ground joint through which fitted an assembly containing an inlet and outlet tube was used. In this flask was placed a carefully weighed 5-g. sample of the carbinol, the flask and contents were placed in an ice-bath and dry hydrogen chloride was passed into the flask until the weight became constant. The lower layer of water saturated with hydrogen chloride was removed with the aid of a capillary, the product was treated with calcium chloride and dissolved hydrogen chloride removed by subjecting the product to evacuation. The product was used directly for the rate measurements without further treatment.

Rate Measurements.—The solvent was made up by mixing 90 parts by volume of acetone with 10 parts by volume of water. It was then adjusted with minor amounts of water or acetone until phenyldimethylcarbinyl chloride yielded a rate constant identical (±2%) with that obtained in the earlier study.[9] Temperatures were controlled to ±0.02° by means of constant temperature baths. The solvent, 100 ml., was placed in long necked 125-ml. flask, brought to bath temperature, and approximately 1 ml. of the halophenyldimethylcarbinyl chloride was added and mixed rapidly with the solvent by vigorous agitation. After 10 minutes a 5-ml. "zero time" sample was removed, placed in 100 ml. of 0° acetone and titrated immediately with 0.0305 N sodium hydroxide solution, using methyl red as indicator. At appropriate intervals of time, six to seven additional 5-ml. aliquots were removed and titrated. To obtain the "infinity" titer, 5-ml. aliquots were removed, added to 100 ml. of 50% aqueous acetone, permitted to stand at room temperature for 24 to 48 hr. and titrated as before. The rate constants were calculated by the usual first-order expression, $k_1 = (2.303/t) \log (a - x_0)/(a - x)$.

The results of a typical determination are summarized in Table IV.

TABLE IV

RATE DATA FOR THE SOLVOLYSIS OF *m*-CHLOROPHENYLDIMETHYLCARBINYL CHLORIDE IN 90% ACETONE AT 25.0°

Time, min.	x, ml.	$a - x$, ml.	$k_1 \times 10^3$, hr.$^{-1}$
0	0.072	9.713	
90	.175	9.610	7.09
400	.510	9.275	6.92
1175	1.315	8.470	6.99
1495	1.610	8.175	6.92
1710	1.810	7.975	6.92
2635	2.625	7.160	6.95
3110	3.025	6.760	6.99
∞	9.785		
		Average	6.97[a]

[a] In a duplicate run, the rate was determined to be 7.02 × 10^{-3} hr.$^{-1}$.

The energies of activation and log A terms were calculated by a least squares treatment of the rate data at several temperatures. The values of the enthalpy and entropy of activation were obtained by an independent least squares analysis of the rate constants utilizing the procedure described by Cagle and Eyring.[16]

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[16] F. W. Cagle and H. Eyring, THIS JOURNAL, **73**, 5628 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Rates of Solvolysis of the Nitro- and the Methoxyphenyldimethylcarbinyl Chlorides[1-3]

BY Y. OKAMOTO AND HERBERT C. BROWN

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o-, *m*- and *p*-methoxyphenyl and *m*- and *p*-nitrophenyldimethylcarbinyl chlorides were solvolyzed in aqueous acetone and the rate data extrapolated to give the rate constants in 90 vol. % acetone at 25°. The *m*-methoxy derivative reacts at a rate 0.6 that of the parent compound but the *para* derivative at a rate of 3360 that of the unsubstituted derivative. The enormous rate increase is a measure of the powerful resonance contribution of the *p*-methoxy group. On the other hand, *m*- and *p*-nitro groups reduce the rate over the parent phenyl derivative by factors of 1150 and 3900, respectively. The ratio of the rate constants for *p*-methoxy and *p*-nitrophenyldimethylcarbinyl chlorides is 10^7, indicating the high sensitivity of this electrophilic reaction to the electronic contributions by the substituents.

In an earlier publication it was proposed that a set of substituent constants, σ^+, could be developed which would permit the quantitative treatment of aromatic substitution.[4] In the first paper of this group it was pointed out that the rates of solvolysis of the phenyl- and tolyldimethylcarbinyl chlorides obeyed the empirical relationship, $\log p_f = 1.310 \log (p_f/m_f)$, which describes the substitution behavior of toluene.[5] This suggested that the rates of solvolysis of the aryldimethylcarbinyl chlorides might provide a convenient experimental route to the desired substituent constants.

In examining this possibility, a study was made

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[1] Directive Effects in Aromatic Substitution. XIII.

[2] Supported by the Petroleum Research Fund of the American Chemical Society.

[3] Based upon a thesis submitted by Y. Okamoto, in 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[4] C. W. McGary, Jr., Y. Okamoto and H. C. Brown, THIS JOURNAL, **77**, 3037 (1955).

[5] H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *ibid.*, **79**, 1897 (1957).