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The Substituent Effect. VIII. Solvolysis of *m*- and *p*-Substituted α-Methylbenzyl Chlorides

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The rates of solvolysis of twenty-two *m*- and *p*-substituted α-methylbenzyl chlorides were determined in 80% aqueous acetone. The relative rates at 45 °C are not correlated linearly with σ^0 or σ. The use of Brown's σ^+ improves the fit but the resulting correlation is still concave. An excellent correlation, $\log k/k_0=-4.950\ (\sigma^0+1.147\,\Delta\bar{\sigma}_R{}^+)$, was obtained by applying the LArSR equation. The r value 1.15 suggests that the π-electronic contribution relative to the inductive contribution of $-R$ *para* substituents at the transition states differs with reaction, and is more important in the present α-methylbenzyl than Brown's *t*-cumyl solvolysis ($r=1.00$ by definition). A set of $\Delta\bar{\sigma}^+$ and σ^+ corresponding to the substituent constants for unit r were calculated. The calculated σ^+ values are in precise agreement with Brown's primary σ^+ values. The generality of the LArSR equation and some new substituent constants are illustrated.

Although Brown's $\rho\sigma^+$ treatment is successful for describing substituent effects in the solvolysis and aromatic substitutions,[1] there is substantial evidence that the actual blend of inductive and resonance effects varies with reaction.[2,3] Taking this into account, we proposed the equation,

$$\log (k/k_0) = \rho(\sigma^0+r\Delta\bar{\sigma}_R{}^+) \qquad (1)$$

and illustrated its applicability to various electrophilic reactions.[4-6] σ^0 is the normal substituent constant which does not involve any additional π-electronic interaction between substituents and the reaction center. $\Delta\bar{\sigma}_R{}^+$ is the resonance substituent constant measuring the capability for π-electron delocalization of conjugatively electron releasing ($-R$) substituents and is defined by $\sigma_p{}^+-\sigma_p{}^0$. The r parameter is the resonance reaction constant describing the required resonance stabilization of the transition state of given reaction; $r=1.00$ is referred to Brown's $\sigma_p{}^+$ scale and $r=0.00$ to the unexalted $\sigma_p{}^0$ scale. Equation (1) has been employed for various reactivity data.[7,8] In order to confirm the applicability and the possible limitation of our treatment, it is necessary to reconfirm the validity of the required substituent parameters. Since the resonance substituent constant $\Delta\bar{\sigma}_R{}^+$ is based on two reference sets of substituent constants σ^0 and σ^+, our studies have been carried out along two principal lines of reconfirmation of both reference sets of the substituent parameters.[9] For the reexamination of σ^+ as well as $\Delta\bar{\sigma}_R{}^+$, we need data of the effects of a variety of substituents on the solvolytic system similar to Brown's reference reaction. Only a few data were available to test the applicability of Eq. (1). The system to be studied should be a simple reaction having a similar transition state to Brown's system. The solvolysis of *m*- and *p*-substituted α-methylbenzyl chlorides was chosen for study. The kinetic data of this series appear to be important in connection with the comparison of substituent effects in secondary and tertiary carbonium ion reactions. Results of several less extensive studies on this system are available,[10-12] but none are satisfactory.

We carried out kinetic studies of the solvolysis of various series of substituted arylmethylcarbinyl chlorides in various solvents. Parts of the results have been reported.[6,13,14] Several sets of interesting data of similar kinetic studies have also been reported.[14-16] A complete set of our data is presented with a discussion in comparison with the relevant data. Our studies include the solvolysis of substituted phenyl-, α-naphthyl,[17] 3′- and 4′-substituted biphenyl-,[18a] and 7-substituted 2-fluorenyl-[18b] derivatives.

The present paper is concerned with the substituent effects on the solvolysis of *m*- and *p*-substituted α-methylbenzyl chlorides in 80% aqueous acetone.

Results and Discussion

The rates of solvolysis of *m*- and *p*-substituted α-methylbenzyl chlorides were determined in 80% aqueous acetone at convenient temperatures to give moderate rates for respective derivatives. All the runs followed accurately the first order kinetic law, the rate constants being obtained with accuracy of 1%, except for *p*-methoxy derivative. Rate constants (Table 1) are in good agreement within the usual accuracy with the values in literature. Extrapolation of these data was made solely by means of the Arrhenius equation at 45 °C. The relative rate varies remarkably with substituent changes over a range of six powers of ten, and the reactivities for both the highest and lowest ends are not presumed to be less reliable. Especially for *p*-methoxy derivative a rather large uncertainty will be expected because of experimental difficulties in measuring the rapid reaction at extremely low temperatures and uncertainty in the extrapolation to 45 °C. *m*-Halogen derivatives may also involve somewhat large uncertainty because of extrapolation from measurements at temperatures higher than the boiling point of the solvent. From remarkable divergence of the reactivities, however, minor errors involved are not expected to affect the following discussion of the substituent effect. Logarithms of relative rates at 45 °C are linearly correlated in excellent precision ($s=\pm 0.030$, $R=0.9999$) with those at 25 °C giving a slope of 0.9615. The same

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TABLE 1. SOLVOLYSIS RATES OF m- AND p-SUBSTITUTED α-METHYLBENZYL CHLORIDES IN 80% AQUEOUS ACETONE

Subst.	Temp. °C	10^5k s^{-1}	$(k/k_0)_{45°\mathrm{C}}$	E_a kcal mol^{-1}	log A
H	45.00	0.729; 0.733[c]	1.00	22.2	10.14
	55.00	2.13			
	65.00	5.84			
p-CH$_3$O	−30.0	7.89; 8.03[c]	5.8×10^4	17.6	11.69
	−21.0	28.0			
	−15.0	65.6[c]			
	−13.9	77.8			
	45.0	42000[a]			
p-CH$_3$S	−15.0	2.64	3.33×10^3	18.7	11.20
	−10.0	4.77			
	−5.00	9.90			
	0.00	18.8			
	3.00	28.1			
	5.00	34.0			
	10.00	63.1			
	45.00	2430[a]			
p-C$_6$H$_5$O	3.00	8.67	1.23×10^3	19.3	11.19
	10.00	21.1			
	20.00	66.9			
	45.00	894[a]			
2-Fluorenyl	0.00	1.940	554	20.4	11.63
	3.00	3.08			
	12.00	9.69			
	15.00	13.15			
	18.00	19.5			
	25.00	46.5; 47.9[c]			
	45.00	404[a]			
p-CH$_3$	45.00	31.0; 31.8[c]	42.5		
p-C$_2$H$_5$	45.00	24.9	34.2		
p-i-Pr	45.00	19.8	27.2		
p-t-Bu	45.00	14.4	19.8		
p-C$_6$H$_5$	39.65	4.16	10.4	21.5	10.65
	45.00	7.98; 8.57[c]			
	49.75	12.97			
	55.00	20.72			
2-Napht	45.00	5.18; 5.03[c]	7.11		
m-CH$_3$	45.00	1.46	2.00		
p-F	45.00	2.11	2.89		
m-CH$_3$O	55.00	1.26	0.584	22.6	10.16
	70.00	5.87			
	80.00	14.6			
	45.00	0.426[a]			
m-C$_6$H$_5$	70.00	2.96	0.288	23.0	10.14
	80.00	8.72			
	90.00	19.0			
	45.00	0.210[a]			
m-CH$_3$S	70.00	1.81	0.176	23.0	9.91
	80.10	4.76			
	90.00	11.6			
	45.00	0.128[a]			
p-Cl	55.00	0.711	0.331	22.2	9.61
	60.00	1.18			
	70.00	3.14			
	80.00	7.94			
	45.00	0.246[a]			
p-Br	54.90	0.419[c]	0.207	22.9	9.85
	60.00	0.802			
	70.00	2.07			
	80.00	5.06			

Table 1 (continued)

Subst.	Temp. °C	$10^5 k$ s^{-1}	$(k/k_0)_{45°C}$	E_a kcal mol^{-1}	log A
	45.00	0.151$^{a)}$			
p-I	70.00	2.38	0.248	22.5	9.68
	80.00	6.29			
	90.00	14.6			
	45.00	0.181$^{a)}$			
m-F	80.00	0.626	0.0213		
	45.00	0.0155$^{b)}$			
m-Cl	70.00	0.146	0.0133	23.6	9.19
	80.00	0.393			
	90.00	1.53			
	45.00	0.00969$^{a)}$			
m-Br	70.00	0.134	0.0113	24.2	9.53
	80.00	0.366			
	90.00	1.49			
	45.00	0.00826$^{a)}$			

a) Extrapolated from the rate constant at other temperatures by the Arrhenius equation. b) Estimated from the rate constant at 80°C on the basis of linear log *k*-log *k* relation between the rates at 80°C and those at 45°C. c) Average values of repeated determinations.

is true in the log-log plot of relative rates at 45 °C *vs.* those at 80 °C. Thus, an arbitrary choice of the reference temperature 45 °C also does not affect the present discussion, except for the minor temperature effect on the ρ-value.

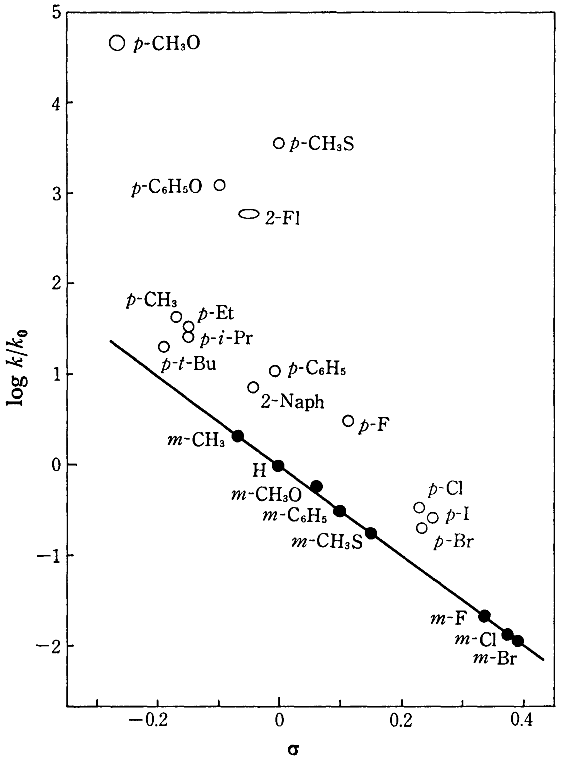

Fig. 1. Hammett plot of the solvolysis of α-methylbenzyl chlorides in 80% aq. acetone at 45 °C.

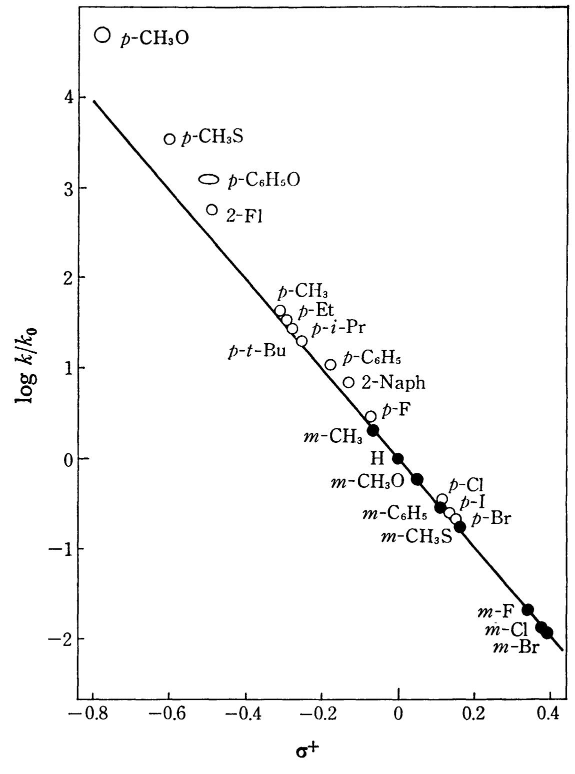

Fig. 2. Hammett-type plot against Brown's σ$^+$.

As anticipated for the typical benzylic S_N1-solvolysis reactions, σ^0 or σ is unable to correlate linearly the present reactivity data as shown by the σ-plot in Fig. 1, in which *meta* substituents fall on a straight line to give a ρ_m value of -4.964 ± 0.025, but all $-R$ *para* substituents deviate upwards from the *meta* line. Brown's σ$^+$ provides a much better correlation (Fig. 2) with a ρ$^+$ value of -5.51 (standard deviation ± 0.17 and correlation coefficient 0.995). The line is not for the best fit correlation but is drawn through the points for *m*-substituents. The best-fit ρ$^+$ value is considerably higher (more negative) than the ρ_m value based on *meta* substituents. Points for weakly conjugative *para* groups appear to fall near the the ρ_m-line, whereas strongly electron-releasing ($-R$) groups, such as *p*-methoxy, *p*-phenoxy, 2-fluorenyl and *p*-methylthio groups, deviate significantly to the direction of enhanced reactivity from the ρ_m-line. Excluding four such faster reacting groups, an improved partial σ$^+$ correlation within a range of substituents from *p*-methyl to *m*-bromo groups can be obtained with correlation coefficient 0.999 and standard deviation ±0.057, to give $\rho^+ = -4.980 \pm 0.060$, which is close to the ρ_m value. This indicates that Brown's $\rho\sigma^+$ treatment can practically be applied to the present reactivity set only within a limited range of weakly conjugative substituent groups. Even though the deviation of *p*-methoxy group might be ascribed to the error in its relative rate at 45 °C due to experimental difficulties, such serious errors are not expected for the rates of *p*-phenoxy and *p*-methylthio-derivatives. Deviation of these substituents should be due to difference in stabilization of the transition states between the present and cumyl system. The overall $\rho\sigma^+$ correlation is represented by a smooth upward curvature.[19] Brown's treatment can not describe adequately the effect of strongly electron-donating *para* substituents in the present reaction.

From the above ρ_m value, we can derive a set of apparent substituent constants ($\bar{\sigma}$) of the σ^+-type from the relative rates of the present solvolysis by

$$\bar{\sigma} = (\log k/k_0)/(-4.964)$$

As an operational definition, this set of apparent substituent constants are completely independent of and should be equivalent in nature to Brown's σ^+ parameters determined by the same procedure from the *t*-cumyl solvolysis rates. The apparent σ values for *m*-substituents, $\bar{\sigma}_m$, agree precisely with Brown's $\bar{\sigma}_m{}^+$, even better than with the standard σ_m values, while the σ values for all $-R$ *para* substituents (Table 2) are consistently more negative than the corresponding Brown's σ^+ values. This suggests that the additional resonance contribution from $-R$ *para* substituents is more important in the transition state of the secondary benzylic carbonium ion structure than in the latter tertiary carbonium ion transition state, and that there is no unique set of σ^+ constants applicable to electrophilic exalted resonance type reactivities. The blend of resonance and inductive effects represented by Brown's σ^+ constants appears to be only a sufficiently good average to fit most cases. The varied contribution of the resonance effect can be taken into account, as a precise approximation, by application of Eq. (1) from which it immediately follows that

$$(\log k/k_0)/\rho = \sigma^0 + r\Delta\bar{\sigma}_R{}^+ \qquad (2)$$

This indicates that the exaltation of apparent $\bar{\sigma}_p$ from σ^0,

TABLE 2. CALCULATED VALUES OF SUBSTITUENT PARAMETERS

Subst.	$\bar{\sigma}$ a)	$(\Delta\bar{\sigma}_R{}^+)_{calcd}$ b)	σ^+_{calcd}	σ^+ d)
p-CH_3O	−0.959	−0.755	−0.855	−0.778
p-CH_3S	−0.709	−0.697	−0.614	−0.604
p-C_6H_5O	−0.622	−0.602	−0.539	(−0.5)
2-Fluorenyl	−0.553	−0.487	−0.486	−0.490
p-CH_3	−0.328	−0.182	−0.306	−0.311
p-C_2H_5	−0.309	−0.160	−0.291	−0.295
p-*i*-Pr	−0.289	−0.120	−0.276	−0.280
p-*t*-Bu	−0.261	−0.080	−0.254	−0.256
p-C_6H_5	−0.205	−0.219	−0.180	−0.179
2-Napht	−0.172	−0.207	−0.145	−0.135
p-F	−0.093	−0.270	−0.058	−0.073
p-Cl	0.093	−0.167	0.114	0.115
p-Br	0.138	−0.141	0.155	0.150
p-I	0.122	−0.157	0.141	0.135
H	0.000	0.000	0.000	0.000

a) Apparent $\bar{\sigma}$ values given by $\bar{\sigma} = \log k/k_0/(-4.964)$; use of $\rho = -4.950$ instead of $\rho_m = -4.964$ does not affect the results. b) Giving by $[\log k/k_0/(-4.950) - \sigma_p{}^0]/1.15$. c) $\sigma^+ = (\Delta\bar{\sigma}^+{}_R)_{calcd} + \sigma_p{}^0$. d) Brown's primary σ^+ values taken from Ref. 1.

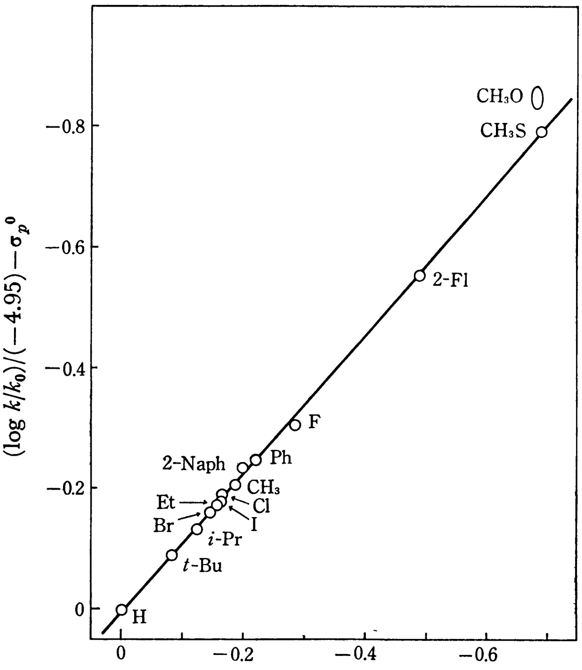

Fig. 3. Plot of the apparent resonance exaltation, $(\log k/k_0)/(-4.95) - \sigma_p{}^0$, in the solvolysis against $\Delta\bar{\sigma}_R{}^+$

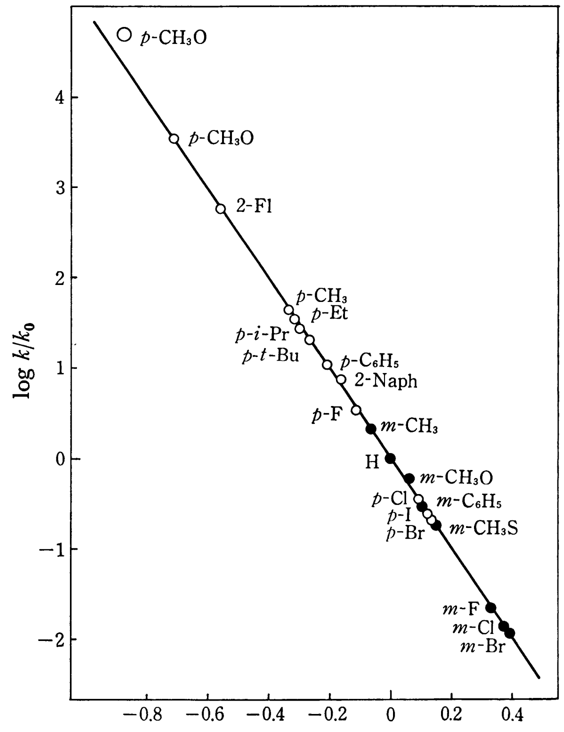

Fig. 4. LArSR plot of the log k/k_0 at 45 °C.

the quantities $(\log k/k_0)/\rho-\sigma^0$, should be proportional to the resonance parameter $\Delta\bar{\sigma}_{\mathrm{R}}^{+}$. Figure 3 illustrates such a plot. The slope should correspond to the *r* value. It is obvious that there is no trend of curvature in the plot but only the *p*-methoxy group clearly deviating from the line. The deviation can be attributed to the error in the relative rate of this group. The linear plot offers confirmation of the validity of our LArSR relationship. The ordinary LArSR plot for the present reaction is shown in Fig. 4. No trend of curvature except for the *p*-methoxy group is indicated. Least squares calculation gives a ρ-value −4.953 and *r* 1.147 excluding *p*-methoxy group (standard deviation ±0.040 and correlation coefficient 0.9997). Substituent constants utilized are given in Table 3. The ρ-value is identical within experimental uncertainty to the ρ_m value based on *m*-substituents alone and appreciably less than that given by the σ^+-resorting. The high *r*-value is consistent with the view that the resonance contribution from $-R$ *para* substituents to the stabilization of the transition state is more important in the present series than in Brown's cumyl system. Putting $r=1.15$ and $\rho=-4.950$ in Eq. (1), we can obtain a calculated set of $\Delta\bar{\sigma}_{\mathrm{R}}^{+}$ values and a secondary set of σ^+ values in Brown's scale $(r=1.00)$. They are compared with Brown's primary values (Table 2). Both sets of σ^+ are in precise agreement within ±0.007 in σ unit for all *para* substituents except the *p*-methoxy group. The rates of solvolysis of several polynuclear arylmethylcarbinyl chlorides under the same conditions[12] have been treated on the basis of the above correlation in order to derive the σ^+ and $\Delta\bar{\sigma}_{\mathrm{R}}^{+}$ constants for these aryl moieties as derivatives of the parent phenyl compound. The applicability of these parameters for other reactions was shown in a previous paper.[13] Kusuyama and Ikeda[14a] recently determined the rates of hydrolysis of *p*-cyclopropyl- and *p*-(β,β-dichloro-cyclopropyl)-α-methylbenzyl chlorides and obtained, on the basis of the above correlation, the σ^+ and $\Delta\bar{\sigma}_{\mathrm{R}}^{+}$ constants for cyclopropyl and β,β-dichlorocyclopropyl groups.[14a] The results are given in Table 4. The σ_p^+ for *p*-cyclopropyl group is consistent with the estimation from the *t*-cumyl reactivity.[14] The particularly large $\Delta\bar{\sigma}_{\mathrm{R}}^{+}$ value of −0.36 as compared with ordinary alkyl groups is striking, and suggests that the donating resonance power of this group is roughly close to that of 2-fluorenyl and much stronger than that of *p*-phenyl or ordinary alkyl groups.

TABLE 3. SUBSTITUENT PARAMETERS

Subst.	σ_m^0	σ_p^0	$\Delta\bar{\sigma}_{\mathrm{R}}^{+}$
CH_3O	0.060	−0.100	−0.678
CH_3S	0.15	0.083	−0.687
C_6H_5O		0.063	
2-Fluorenyl		0.001	−0.491
CH_3	0.069	−0.124	−0.187
C_2H_5		−0.131	−0.164
i-Pr		−0.156	−0.124
t-Bu		−0.174	−0.082
C_6H_5	0.10	0.039	−0.218
2-Napht		0.062	−0.197
F	0.337	0.212	−0.285
Cl	0.373	0.281	−0.167
Br	0.391	0.296	−0.146
I		0.298	−0.163

TABLE 4. ESTIMATION OF SUBSTITUENT PARAMETERS

Substrate	$\bar{\sigma}$[a)]	σ^0[b)]	$(\Delta\sigma_{\mathrm{R}}^{+})_{\mathrm{calcd}}$[c)]	$\sigma^{+}_{\mathrm{calcd}}$[d)]
Phenyl	0.000	0.000	0.000	0.000
4-Biphenylyl	−0.212 −0.209[e)]	0.039	−0.219	−0.180
2-Naphthyl	−0.176 −0.174[e)]	0.062	−0.207	−0.145
2-Phenanthryl	−0.144[e)]	0.131	−0.240	−0.109
3-Phenanthryl	−0.230[e)]	0.109	−0.296	−0.187
2-Fluorenyl	−0.558	0.001	−0.487	−0.486
9-Phenanthryl	−0.197[e)]	0.113	(−0.270)[g)]	(−0.157)[g)]
1-Naphthyl	−0.251[f)]	0.048	(−0.239)[g)]	(−0.191)[g)]
p-*c*-C_3H_5-phenyl	−0.515[h)]	−0.10[h)]	−0.362	−0.462[i)]
p-*c*-$C_3H_3Cl_2$-phenyl	−0.019[h)]	0.05[h)]	−0.06	−0.01

a) Apparent substituent constant given by $\bar{\sigma}=(\log k/k_0)/(-4.950)$. b) Taken from Ref. 13. c) Calculated by $(\bar{\sigma}-\sigma^0)/1.147$. d) $\sigma^{+}_{\mathrm{calcd}}=\sigma^0+(\Delta\bar{\sigma}_{\mathrm{R}}^{+})_{\mathrm{calc}}$. e) Ref. 12. f) Ref. 17. g) The parameter value does not appear to be practically applicable because of the reaction-dependent *peri*-effect. h) Ref. 14a. i) Shechter reported the same value of the primary σ^+ (Ref. 14b).

The σ^+ values for *p*-methylthio, *p*-phenoxy, and 2-fluorenyl have seldom been applied to typical electrophilic reactions and have not yet been examined in detail. For the *p*-phenoxy group even the primary σ^+ value has not been determined. The present results will thus give some support for validity of σ^+ values for these groups. Clementi *et al.* studied the effect of *p*-CH_3S group on electrophilic aromatic substitutions in order to confirm the reliability of the σ^+ value and also illustrated far better results with LArSR treatment of the reactions whose *r* values differ from unity.[20a)]

Equation (2) implies that, as a good approximation, the variation of apparent substituent constants of a given *para* substituent should be a linear function of *r* for varying reaction. The slope of the relation should correspond to the $\Delta\bar{\sigma}_{\mathrm{R}}^{+}$ and the intercept to the σ^0 of the substituent.

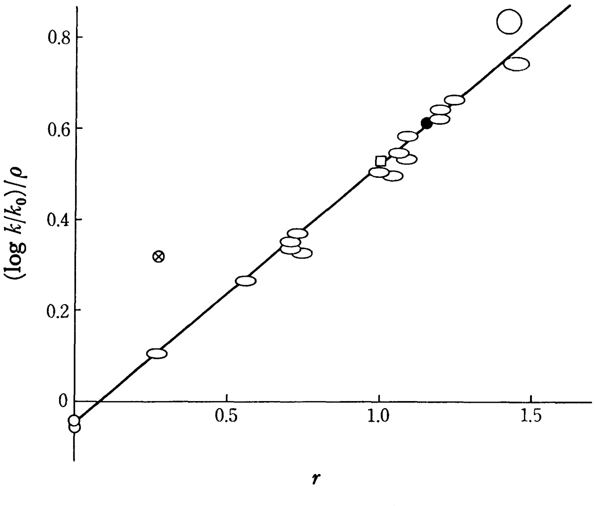

Fig. 5. Plot of the apparent substituent constants, $\bar{\sigma}=(\log k/k_0)/\rho$, for *p*-phenoxy group against *r*.
●: present study, □: $\sigma^{+}_{\mathrm{calc}}$, ⊗: pK_a of benzoic acids.

Ordinary substituents satisfy this relation.[5] Figure 5[20c] shows the plot for *p*-phenoxy group. Both $\Delta\bar{\sigma}_R^+$ and σ^0 for this group estimated from this correlation are in good agreement with the above values, suggesting its applicability to various reactions. Similarly good correlations are obtained for *p*-phenyl and 2-fluorenyl derivatives.[5,13]

The *p*-methoxy group is in most cases the only substituent which has a particularly large $\Delta\bar{\sigma}_R^+$ value as compared with other ordinary substituents, such as alkyls and halogens. The best fit correlation should thus be determined most effectively by the *p*-methoxy group and might be constrained by the error involved in its reactivity. Since the above three groups, *p*-CH_3S, *p*-C_6H_5O, and 2-fluorenyl, are sufficiently stable under ordinary solvolytic conditions, use of these groups may be recommended as a good alternative of *p*-methoxy group for the correlational analysis of substituent effects and as auxiliary substituents for estimation of $-R$ resonance requirement of given reactions.

The point for the pK_a of benzoic acids in Fig. 5 deviates seriously from the correlation line, while the points for the saponification of benzoic esters and other σ-type reactivities having the comparable *r*-value (round 0.28) fall on the line. This suggests a limited applicability of the σ-value—0.32, recommended by Brown and McDaniel.[21] The σ value of −0.10 derived from the hydrolysis of substituted ethyl benzoates in aq. ethanol[22] is in accord with the calculated value from the above correlation (Fig. 5).

Another fact of interest is observed in the behavior of *p*-phenyl substituent. The lower $\Delta\bar{\sigma}_R^+$ value of *p*-phenyl group, or the smaller slope in the apparent $\bar{\sigma}$ *vs.* *r* plot, than that of 2-fluorenyl indicates a considerable decrease in the transition state resonance due to the deviation from the coplanarity of both benzene rings in the former. Stock and Brown suggested,[23] on the basis of their observation of a non-linear selectivity relation for *p*-phenyl but for fluorenyl derivatives in electrophilic aromatic substitutions, that the substituent phenyl-ring in the former should be forced to lie in a nearer coplanarity to get a maximum possible overlap of both π-systems as the demand of donative resonance of the reaction site becomes larger. On the other hand, Neuman pointed out that the log p_f for 2-fluorenyl was at least as good a linear function of log p_f for *p*-phenyl as that for *p*-methyl, and that the fluorenyl did not fit the selectivity relation much better than *p*-phenyl group.[24] Deviations in these relations were quite large in both plots and the failure of Brown's selectivity treatment is partly associated with variations of *r*-value. It may be expected that the twisting causes certain failure in the $(\log k/k_0)/\rho$ *vs.* *r* correlation for phenyl group. Since *r* can be regarded as a measure of the demand of resonance of the reaction site, the coplanarity of both phenyl rings may increase as the *r* increases, and cause a parallel increase in the resonance power ($\Delta\bar{\sigma}_R^+$) of phenyl group to approach the $\Delta\bar{\sigma}_R^+$ for 2-fluorenyl. No such effect is detectable in the present treatment, the plot for phenyl being as precisely linear against *r* as that for fluorenyl derivative. *p*-Phenyl group appears thus to be a well-behaving $-R$ substituent in the usual electrophilic reactions. As far as the ordinary solvolysis and aromatic electrophilic substitution reactions are concerned, the changes in the electron deficiency of reactions cause no significant changes in the twisting angle of the biphenyl at the transition states of varied reactions.

We see that the LArSR equation can describe the present reaction far more precisely than Brown's $\rho\sigma^+$ treatment. However, a sophisticated treatment with an additional term should give more satisfactory results than the simpler treatment. From a practical point of view the simpler $\rho\sigma^+$ treatment can provide satisfactory correlation for the present system within the limit of usual accuracy of linear free energy relationships. This is not inconsistent with the significance of the additional resonance parameter, because we have chosen the present reaction as the reference reaction mechanistically close to Brown's reference reaction. Essentially a small difference in the *r*-value between the present and Brown's reference reactions may not result in significant improvement of the correlation with the LArSR treatment.

Brown estimated the secondary σ^+ values for polynuclear aryl moieties from the solvolysis of α-arylethyl chlorides,[12] on the basis of a linear log *k*–log *k* relation of 4 common derivatives.[25] The σ^+ values compared in Table 4 are in good agreement with ours. The σ^+ treatment seems to be practically applicable to the solvolysis of α-arylethyl chlorides including these polynuclear aryl derivatives, even if the applicability might be limited in the choice of substituents as well as in accuracy. Streitwieser *et al.*[16] demonstrated the applicability of a set of σ^+ for these moieties to several benzylic carbonium ion reactions. The σ^+ was applied to the desilylation of aryltrimethylsilanes[26] and also to the pK_{BH^+} of aryl methyl ketones.[13] The results support Brown's single σ^+ treatment, as a practical approximation of the simple linear free energy relationship, in a broad range

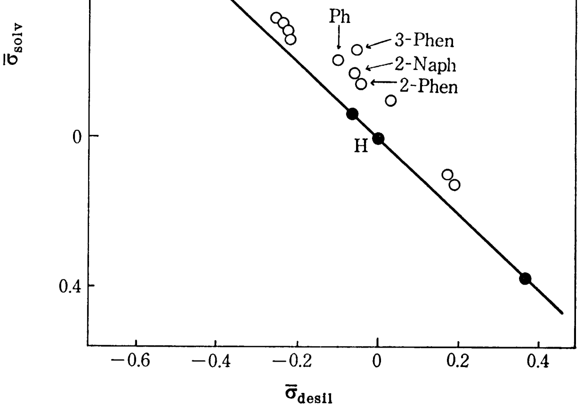

Fig. 6. Correlation of the apparent substituent constants between the present solvolysis and protodesilylation.

of electrophilic type conjugation reactions. We are not concerned here with the difference in the precision of fit with Eq. (1) and Brown's basis treatment, since introduction of more parameter should inevitably improve the precision of fit. Nevertheless, it must be pointed out that even through the σ^+ treatment is valid as a practical approximation both for the present solvolysis and the desilylation, the $\bar{\sigma}$ values from both reactions can not correlate linearly with each other (Fig. 6), giving a quite similar pattern to that in Fig. 1. $-R$ *para* substituents as well as polynuclear aryls in Fig. 6 deviate more or less seriously from the *meta*-correlation line, apparently depending upon their resonance capabilities. The partial correlation with respect to polynuclear aryls is of poor quality. This arises from the significant difference in the *r* values of both reactions 0.7 and 1.15. The correlation between $\mathrm{p}K_{\mathrm{BH}^+}$ of aryl methyl ketones and the present solvolysis is much the same as above.

σ^+ appears to be the best average to fit most cases and practically applicable within satisfactory precision to the electrophilic reactions having *r* value in the range 0.8—1.2, while a definite set of σ^+ can not describe the substituent effect in the reaction having the *r* value outside of this range. Examples are the acetolysis of neophyl brosylates[27] and *β,β*-diarylethyl tosylates[28] and the like which require *r* of about 0.5. The *r*-parameter has been verified to be a useful measure of the degree of resonance contribution from substituents in the rate determining transition state and is applicable to the estimation of the electronic structure of transition states. In a comparison of the solvolysis of benzyl, α-methylbenzyl, and *t*-cumyl chlorides, the *r* parameter appears to decrease in the order, 1.5 (approximate value), 1.15, and 1.00 as the number of α-methyl substitution increases.[6] The increased stabilization of the charged reaction center at the transition state by the α-methyl group should cause decreased demand of the electron releasing resonance contribution from *para* substituents. This predicts the above decreasing order of *r*-values. The distinctly low *r*-value for acetolysis of neophyl brosylates and the related derivatives might indicate the different mechanism of stabilization of the rate determining transition state from that of ordinary benzyl-type carbonium ion reactions.

As a possible factor affording a higher *r* value in the present reaction, we can not rule out the gradual change in the mechanism within respective series due to incursion of the S_N2-type solvent participation. This effect is observed in the case of substituted benzyl tosylates, for which our treatment fails.[5,6] The solvolysis of α-methylbenzyl chlorides is also a borderline case. The nucleophilic solvent participation might play an important role in the reaction of derivatives carrying stronger electron attracting substituents. The monotonic change in mechanism from limiting S_N1 to non-limiting solvolysis can be expected as the substituent becomes more electron attracting. If this is the case, the σ^+ plot might be monotonically concave upwards and subsequently a lower ρ value given by slow solvolyzing substituents may afford a higher *r*-value. For such a case, the LArSR equation provides a less precise correlation or none at all as an extreme case.[5,6] Evidently this is not the present case.

From the α-deuterium kinetic isotope effect on the solvolysis of substituted α-methylbenzyl chlorides, Shiner *et al.* suggested that derivatives faster solvolyzing than the unsubstituted were solvolyzed by the limiting mechanism but the reaction of *m*-bromo derivative which had a lower isotope effect should involve the S_N2 character to a certain extent.[15] In contrast, there is no consistent trend in LArSR correlation which might point to mechanistic change related to the substituent change. An excellent quality of the correlation leads to the conclusion that no serious change in mechanism is involved in the present solvolysis in this medium, at least down to *m*-halogen substituted derivatives. The constant isotope effect for faster reacting derivatives suggests that the deviation of *p*-methoxy derivative observed in Fig. 4 is not due to change in mechanism. The lower isotope effect value for *m*-bromo derivative of course does not indicate complete loss of the S_N1 character. Even though the incursion of S_N2 mechanism may be the case, we believe that the influence of concurrent S_N2 to the solvolysis rate is negligible in this group and throughout a series of substituents we examined. Determination of the reactivity should be extended further to the derivatives substituted by more strongly electron attracting groups than *m*-halogen.

Since the S_N2 process or the nucleophilic solvent participation depends on both the nucleophilicity and the ionizing power of the solvent, the effect of solvent changes on the correlation should provide important evidence for the above consideration. However, no noticeable effect was observed by changing solvents from 90% to 50% aqueous acetone, in the correlation of the substituent effects within the same range of substituents.[29] The data of Mechelynch-David and Fierens in less nucleophilic aqueous dioxane–formic acid[10] give a linear free energy correlation with the present data. The acetolysis rates also can be correlated by Eq. (1), giving an *r* higher than unity.[30] Thus, the high *r* value is characteristic of the transition state of this reaction. This is further supported by the fact that pyrolysis rates of α-methylbenzyl chlorides are correlated linearly to the present data. No irregularity was observed even in the behavior of strongly electron-attracting *p*-cyano derivative.[31] A strictly linear correlation by Eq. (1) may be taken as a criterion for the operation of a unique mechanism throughout the series of substituted members included.

Experimental

Acetophenones were obtained by the usual Friedel-Crafts acetylation of appropriate substituted benzenes. *m*-Bromoacetophenone was obtained by the bromination of acetophenone in the presence of anhydrous aluminum chloride. *m*-Methoxyacetophenone (bp 135—137 °C/20 mmHg) was obtained by treating *m*-hydroxyacetophenone with dimethyl sulfate in an alkaline solution. *m*-Methylthioacetophenone (bp 127—128 °C/2 mmHg) was prepared by converting *m*-aminoacetophenone with potassium ethylxanthate into the thiophenol, and treating with dimethyl sulfate.

α-Methylbenzyl Alcohols. Acetophenones were reduced with lithium aluminum hydride to the corresponding α-

TABLE 5. MELTING AND BOILING POINTS OF SUBSTITUTED α-METHYLBENZYL ALCOHOLS AND THE CHLORIDES

Subst.	α-Methylbenzyl alcohol		α-Methylbenzyl chloride	
	observed a)	lit. value	observed a)	lit. value
p-OCH$_3$	81°/0.7mm	109—110°/2.5mm 32)	b)	
p-SCH$_3$	105°/0.55mm (47—48°)	(38—40°) 33)	(59—59.5°)	
p-OC$_6$H$_5$	145—147°/2mm	138—140°/0.7mm 15) 160—162°/2mm 34)	b)	
2-Fluorenyl	(138—138.5°)	(139—140°) 35)	(92—93°)	(90.5—92.0°) 39)
p-CH$_3$	103°/15mm	102—103°/11mm 36)	64°/3mm	92°/12mm 36)
p-C$_2$H$_5$	131—132°/25mm	120°/14mm 37)	70°/4mm	152°/80mm 46)
p-*i*-C$_3$H$_7$	95°/3.5mm	127—129°/15mm 38)	81°/4mm	180°/176mm 46)
p-*t*-C$_4$H$_9$	104°/4mm	149—153°/30mm 27)	88°/4.5mm	179°/130mm 46)
p-C$_6$H$_5$	(97°)	(96.4—97.5°) 39)	(52.0—52.5°)	(52.6—53.7°) 39)
2-Napht	(74°)	(71.3—72.1°) 39)	(68°)	(66.4—67.3°) 39)
p-F	90°/10mm	91°/10mm 40)	47—48°/4.2mm	75°/10mm 36)
H	70°/5mm	93°/16mm 41) 106°/20mm 36)	51—52°/6mm	75°/15mm 36)
m-CH$_3$	76°/3.5mm	103—105°/6mm 42)	61°/3.8mm	69—73°/2.5mm 36)
m-OCH$_3$	103—103.5°/1mm	115—120°/5.5mm 43)	73°/1mm	
p-Cl	93.5°/4.5mm	99°/5mm 42)	64°/1.5mm	105°/10mm 36)
m-C$_6$H$_5$	163—165°/3mm	146—149°/1mm 44)	147—148°/2mm	
p-I	(50.5—51.5°)	(40°) 45)	92°/0.4mm	
p-Br	114—115°/5 mm	128°/10mm 36)	89.5—90.0°/3mm	72°/1mm 36)
m-SCH$_3$	125—126°/1.5mm		100°/0.25mm	
m-F	121—122°/4.5mm		64.5—66.5°/6—6.5mm	
m-Cl	95°/4mm	99—104°/4mm 42)	72—73°/5mm	
m-Br	91—92°/2.5mm	108—110°/2mm 42)	66—67°/1.5mm	

a) Boiling point °C (uncorrected) under a given pressure, mmHg. Mp's are given in brackets. b) Used without purification.

arylethyl alcohols in 80—90% yields by the usual procedure. *m*-Methyl, *m*-phenyl, *m*-fluoro, and *m*-chloro-α-methylbenzyl alcohols were prepared by the Grignard reaction of the corresponding bromobenzenes with acetaldehyde in about 60% yields. They were purified before being converted into chlorides by distillation under reduced pressure or recrystallization from petroleum benzine. The physical constants of alcohols are summarized in Table 5.

α-Methylbenzyl Chlorides. Most *m*- and *p*-substituted α-methylbenzyl chlorides, α-(2-fluorenyl)ethyl chloride and α-(2-naphthyl)ethyl chloride were prepared by the following method. The alcohol in ether containing anhydrous calcium chloride was treated under cooling in an ice-bath with a stream of dry hydrogen chloride, through a concd. sulfuric acid trap, and the resulting solution was decanted and treated with hydrogen chloride in the presence of fresh anhydrous calcium chloride for *ca.* 3 h. The ether was removed under reduced pressure and the residue was purified by fractionation through a column or recrystallized from appropriate solvents. *p*-Methoxy and *p*-phenoxy-α-methylbenzyl chlorides were used without further purification for kinetic measurements immediately after evaporation of ether as completely as possible, since they were quite unstable. Unsubstituted and *m*- and *p*-halo-substituted and *m*-methoxy, *m*-phenyl and *m*-methylthio-α-methylbenzyl chlorides were obtained by the following procedure. Benzene solution of α-methylbenzyl alcohol (1 equivalent) was dropwise added with stirring into a benzene solution of thionyl chloride (2 equivalent). The mixture was kept overnight, and evaporated under reduced pressure. The residue was purified by distillation under nitrogen *in vacuo* (yield, 70—80%). Physical constants of the chlorides are summarized in Table 5. Chlorides were prepared in small portions each time before use. Some stable chlorides were stored in a refrigerator in sealed ampoules and were repurified before use.

Solvent. 80% aqueous acetone was prepared by mixing 8 volumes of purified acetone and 2 volumes of distilled water. Different batches of solvent were standardized each time by adding a small amount of water or acetone to give an identical solvolysis rate for the reference sample.

Kinetic Measurement. The procedure of the rate determination is essentially the same as that described by Brown and Okamoto.1) The reaction temperature was controlled within ±0.01 °C in the range 15—18 °C, and ±0.02 °C or less at temperature outside of this range; very low temperature was estimated to be less accurate than ±0.1 °C. The rate studies were carried out by using freshly prepared or repurified samples before each run. Measurements at temperatures 10—30 °C were carried out in a long-necked flask with a ground joint stopper. A weighed amount of chloride was quickly dissolved in a small amount of the solvent and made up to the volume corresponding to 0.02 M with the solvent preheated to the reaction temperature in a volumetric flask, shaken vigorously and transferred to a reaction flask immersed in a thermostated bath. At appropriate time intervals, 10 ml aliquots were quenched by pouring into ice-cold acetone (50 ml) and the hydrochloric acid liberated was titrated with aqueous sodium hydroxide solution (*ca.* 0.03 M). Bromocresol purple was used as an indicator. The initial concentration was obtained from the infinity reading determined after 10 half-lives of the reaction. Measurements above 30 °C for slow reacting chlorides were carried out in sealed ampoules. Ten ml aliquot was used for each determination. Two of the sealed ampoules were allowed to react for at least 10 half-lives, or for the corresponding period at higher temperature, in order to get the infinity reading. Reactions were followed to 75% completion or more, during which period generally more than ten determinations were made. The reaction followed first order kinetics in all cases for two half-lives and in optimum case for up to three half-lives, except the reaction of *p*-methyl derivative, in which a certain drop took place in the first order reaction rate with time. Lewis *et al.* reported a similar phenomenon but gave no clear reason.[11] The experimental errors in respective runs were generally less than 1.0% and correlation coefficients were better than 0.999. Rate constants from repeated runs were reproducible within an accuracy 1.5%. During the course of studies for several years, determinations were made repeatedly by different workers using different samples of the halide in different batches of the solvent. Nevertheless, the repeated runs gave mostly identical rate constants within the limit of our estimated accuracy. The rate constant 3.10×10^{-4} for *p*-methyl (obtained by Y. K. who carried out most measurements) was in agreement with average 3.18×10^{-4} of nine repeated runs by the others.

For the measurements below 10 °C for faster reacting chlorides aliquots were quenched with a large amount of dry ice cold acetone and titrated with aqueous ethanolic sodium hydroxide solution (*ca.* 0.03 M). Titration in a very cold (*ca.* −50 °C) less aqueous solution suffered from the slow response of indicator and the end point could hardly be determined. Rapid titration at an allowable high temperature and the use of a mixed indicator, bromocresol green—methyl red (3:2), were more favorable. The rate constants for the most reactive *p*-methoxy derivative at low temperatures were less accurate. Respective runs gave good first order rate plots of the order of correlation coefficient not less than 0.99. The rate constants from 7 repeated runs at −30 °C agreed within a range of ±4%. The rate constant extrapolated to 45 °C is estimated for this derivative to be of ±10% uncertainty.

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