# Correlation of Rates of Solvolysis for Tertiary Methyl with Tertiary Benzylic Derivatives

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A linear free energy relationship, log $(k/k_0) = \rho\gamma^+$, with group constants, $\gamma^+$, was defined. The group constants are characteristic of the ability of a group to stabilize an adjacent cationic center. These groups can be either aromatic or nonaromatic. The $\gamma^+$ for methyl was determined to be 0.77. This group constant was found to be generally applicable in correlating rates of solvolysis of tertiary methyl derivatives with the analogous tertiary benzylic derivatives. Indeed, excellent $\rho\gamma^+$ plots were obtained. However, in cases with bulky substituents at the reaction center of arylcarbinyl systems, nonlinear $\rho\gamma^+$ plots were obtained. This was attributed to steric inhibition of resonance.

Among the most striking developments in the history of physical organic chemistry has been in methods for the quantitative correlation of rate and equilibrium constants.[1] Such approaches are based on the correlation of relative reactivities in terms of relative free energy changes. One of the best known and most useful of these is an equation proposed by Hammett which relates equilibrium and rate constants for the reactions of meta- and para-substituted benzene derivatives.[1,2] The Hammett relationship is based on the fact that as the substituent is varied, the logarithms of the rate constants for aromatic side-chain reactions are linearly related to one another. Thus, a rate or equilibrium constant of a compound in a reaction is related to the rate or equilibrium constant for the unsubstituted compound in terms of two parameters, $\rho$ and $\sigma$. In the case of rate constants the relationship is shown in

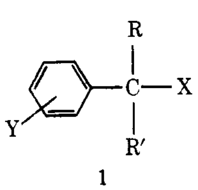
$$\log \frac{k}{k_0} = \rho\sigma \tag{1}$$

where $k_0$ is the rate constant for the unsubstituted compound. Of these two parameters, the substituent constant $\sigma$ is characteristic only of the substituent on an aryl group, while $\rho$ is a reaction constant and is a function of the reaction being considered. Thus the reaction constant or $\rho$ value is a measure of the sensitivity of a particular reaction to the substituents.

The Hammett equation fails when a full positive charge is developed on the aromatic side chain; an example is the solvolysis of benzyl derivatives. However, Brown and co-workers developed an analogous expression which overcame these shortcomings.[3] Thus in the Hammett–Brown relationship (eq 2), $\sigma^+$ represents the resonance and inductive contributions of a substituent on an aryl group in a reaction where a full positive charge is developed during the course of the reaction.

$$\log \frac{k}{k_0} = \rho\sigma^+ \tag{2}$$

The use of $\sigma^+$ constants has been found to be generally applicable to a number of systems.[3c] In particular, Brown, Gassman, Tanida, and other workers have investigated the rates of solvolysis of various tertiary benzylic systems, **1**.



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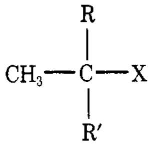
Solvolysis of the analogous tertiary methyl derivatives, **2**, has been reported; however, a method for correlating **2** with **1** is lacking.



$$CH_3-\overset{\displaystyle R}{\underset{\displaystyle R'}{C}}-X$$

2

Recently the correlation of rates of acetolysis of secondary tosylates with tertiary benzylic derivatives by a linear free energy relationship was reported.

This relationship uses group constants, $\gamma^+$, which are characteristic of the ability of an entire group (i.e., aryl, hydrogen, etc.) to stabilize an adjacent cationic center.[4] The $\sigma^+$ values only represent substituents on aryl groups. The $\gamma^+$ values for aryl groups will be the same as the $\sigma^+$ values for the substituent on that aryl group. This linear free energy relationship for correlating aromatic with nonaromatic derivatives is represented by eq 3.[4]

$$\log \frac{k}{k_0} = \rho\gamma^+ \tag{3}$$

Since the difference between **1** and **2** is a methyl group vs. an aryl group, a group constant for a methyl group is needed to correlate tertiary methyl derivatives with their analogous tertiary benzylic derivatives.

## Results

In attempting to correlate such a diverse assortment of data from the literature one might expect some deviation due to the facts that the rate constants were determined in several laboratories, uncertainties arise from extrapolating the rate constants for unreactive derivatives from high temperatures to 25 °C, and the corrections for differences in solvent may vary from system to system. However, these items can be minimized in the determination of $\gamma^+$ for methyl by plotting $-\log (k_{\text{methyl}}/k_{\text{phenyl}})$ vs. the $\rho$ values (calculated from the aryl derivatives alone) for a series of chlorides and $p$-nitrobenzoates.[5] By definition the slope, of this line, $\gamma^+_{CH_3}$, should be made to go through the origin. The observed and calculated values of $-\log (k_{\text{methyl}}/k_{\text{phenyl}})$ and $\rho$ values of just the aryl derivatives are listed in Table I. The slope of this data was analyzed by regression analysis and found to be $0.77 \pm 0.03$ with a confidence level of 99.5 ($F$ distribution and $t$ distribution).

**Solvolysis of Chlorides.** The solvolytic rates for 1-aryl-1-cyclopentyl, 1-aryl-1-cyclohexyl, 2-aryl-2-adamantyl, 1-aryl-1-cyclobutyl, and 7-aryl-7-norbornyl chlorides were correlated with 1-methyl-1-cyclopentyl, 1-methyl-1-cyclohexyl, 2-methyl-2-adamantyl, 1-methyl-1-cyclobutyl, and 7-methyl-7-norbornyl chlorides, respectively. The rates of solvolysis of the tertiary benzylic chlorides in 90% acetone were determined by Tanida and Tsushima.[6] The rates of

Table I. Correlation of Rates of Tertiary Methyl with Tertiary Benzylic Derivatives[a]

| System | $n$[b] | $\rho$ without $CH_3$ | $-\log (k_{CH_3}/k_{phenyl})$ Obsd | Calcd | Dif | SD[c] | $\rho$ with $CH_3$[d] | Corr. coeff.[d] |
|---|---|---|---|---|---|---|---|---|
| Chlorides in 90% Acetone | | | | | | | | |
| Cyclopentyl | 5 | −4.10[e] | 3.1421 | 3.1626 | −0.0205 | 0.1386 | −4.09 | 1.000 |
| Cyclohexyl | 4 | −4.65[e] | 2.6716 | 3.5869 | −0.9153 | 0.1573 | −4.03 | 0.987 |
| 2-Adamantyl | 4 | −4.83[e] | 2.5607 | 3.7257 | −1.1650 | 0.1633 | −4.24 | 0.980 |
| Cyclobutyl | 5 | −4.48[e] | 3.4921 | 3.4557 | 0.0364 | 0.1514 | −4.49 | 1.000 |
| 7-Norbornyl | 4 | −5.64[e] | 4.5867 | 4.3505 | 0.2362 | 0.1906 | −5.75 | 1.000 |
| 2-Propyl | 10 | −4.54[f] | 2.9747 | 3.5020 | −0.5273 | 0.1535 | −4.43 | 0.998 |
| Chlorides in Ethanol | | | | | | | | |
| 2-Propyl | 3 | −4.90[g] | 2.5800 | 3.7797 | −1.1997 | 0.1656 | −4.51 | 0.991 |
| Cyclopentyl | 3 | −4.50[g] | 3.5243 | 3.4712 | 0.0531 | 0.1521 | −4.47 | 1.000 |
| 2-*exo*-Norbornyl | 3 | −4.30[g] | 3.8327 | 3.3169 | 0.5158 | 0.1453 | −4.36 | 0.998 |
| *p*-Nitrobenzoates in 70% Dioxane | | | | | | | | |
| 7-Norbornyl | 6 | −5.25[h] | 4.6517 | 4.0497 | 0.6020 | 0.1775 | −5.31 | 0.999 |
| 7-*anti*-Norbornenyl | 4 | −2.30[i] | 0.9788 | 1.5736 | −0.5948 | 0.0690 | −2.17 | 0.985 |
| *p*-Nitrobenzoates in 80% Acetone | | | | | | | | |
| Cyclopentyl | 4 | −3.82[j] | 3.0904 | 2.9466 | 0.1438 | 0.1291 | −3.88 | 0.998 |
| $\Delta^3$-Cyclopentenyl | 4 | −3.92[k] | 3.7447 | 3.0238 | 0.7209 | 0.1325 | −4.11 | 0.991 |
| 3-Nortricyclyl | 4 | −3.27[l] | 2.3080 | 2.5224 | −0.2144 | 0.1105 | −3.24 | 0.999 |
| 2-*exo*-Norbornyl | 4 | −3.83[j] | 2.8794 | 2.9543 | −0.0749 | 0.1295 | −3.84 | 1.000 |
| 2-*endo*-Norbornyl | 4 | −3.75[j] | 3.6716 | 2.8926 | 0.7790 | 0.1268 | −3.90 | 0.994 |
| 2-*exo*-Norbornenyl | 3 | −4.21[m] | 3.4214 | 3.2475 | 0.1739 | 0.1423 | −4.13 | 0.998 |
| 2-*endo*-Norbornenyl | 3 | −4.17[m] | 4.0600 | 3.2166 | 0.8434 | 0.1409 | −4.49 | 0.995 |
| 5-Methyl-2-*exo*-norbornenyl | 2 | −3.28[n] | 2.2034 | 2.5301 | −0.3267 | 0.1109 | −3.05 | 0.999 |
| 5-Methyl-2-*endo*-norbornenyl | 3 | −4.19[n] | 4.1518 | 3.2320 | 0.9198 | 0.1416 | −4.52 | 0.995 |

[a] Rate constants at 25 °C. [b] Number of aryl derivatives correlated. [c] Standard deviation of calculated $-\log (k_{CH_3}/k_{phenyl})$. [d] Computer calculated using least-squares program. [e] Reference 6. [f] Reference 3. [g] Reference 12. [h] Reference 4. [i] Reference 11. [j] Reference 16. [k] Reference 18. [l] Reference 21. [m] Reference 23. [n] Reference 25.

solvolysis of 1-methyl-1-cyclopentyl, -cyclohexyl, and -cyclobutyl chlorides were determined in 80% ethanol by Brown and Borkowski[7] and corrected to 90% acetone ($5.21 \times 10^{-6}$, $4.18 \times 10^{-8}$, and $8.83 \times 10^{-9}$ s$^{-1}$, respectively) by multiplying the rate constant in 80% ethanol by the factor $1.42 \times 10^{-2}$.[8] The rate of 2-methyl-2-adamantyl chloride[9] was similarly obtained ($1.26 \times 10^{-6}$ s$^{-1}$). The rate constant for 7-methyl-7-norbornyl chloride in 90% acetone ($1.03 \times 10^{-12}$ s$^{-1}$) was calculated by multiplying the rate of acetolysis for the corresponding tosylate[10] by the factor $3.17 \times 10^{-7}$.[11] The data give excellent correlations.

The rates of ethanolysis of 2-aryl-2-propyl, 1-aryl-1-cyclopentyl, and 2-aryl-2-*exo*-norbornyl chlorides[12] were correlated with their anologous methyl derivatives.[13] All three sets of data give excellent correlations with $\gamma^+$ constants. The reaction constants follow: 2-propyl, −4.51 (correlation coefficient 0.991); 1-cyclopentyl, −4.47 (1.000); and 2-*exo*-norbornyl, −4.36 (0.998).

***p*-Nitrobenzoates.** The rates of solvolysis of 7-methyl-7-norbornyl[14] and 7-methyl-*anti*-7-norbornenyl *p*-nitrobenzoates[15] correlate with their 7-aryl analogues.[11] For the saturated series, $\rho$ was −5.31 (correlation coefficient 0.999). For the 7-norbornenyl derivatives, a sharp break in the $\rho\gamma^+$ plot occurs at the *p*-anisyl derivative. For the five compounds (i.e., excluding the *p*-dimethylaminophenyl derivative), $\rho$ was −2.17 (correlation coefficient 0.985).

Several tertiary cyclic, bicyclic, and tricyclic *p*-nitrobenzoates have been studied by Brown and co-workers. Thus rates of solvolysis in 80% acetone for the methyl and benzylic derivatives gave good to excellent correlations with $\gamma^+$. The $\rho$ values are −3.88 (correlation coefficient 0.998) for cyclopentyl,[16,17] −4.11 (0.991) for $\Delta^3$-cyclopentenyl,[18,19] −3.24 (0.999) for 3-nortricyclyl,[20,21] −3.84 (1.000) for 2-*exo*-norbornyl,[16,22] −3.90 (0.994) for 2-*endo*-norbornyl,[16,22] −4.13 (0.998) for 2-*exo*-norbornenyl,[23,24] −4.49 (0.995) for 2-*endo*-norbornenyl,[23,24] −3.05 (0.999) for 5-methyl-2-*exo*-norbornenyl,[16,25] and −4.52 (0.995) for 5-methyl-2-*endo*-norbornenyl.[16,25]

Thus the use of $\gamma^+$ for the methyl group appears generally applicable to a variety of systems.

**Steric Hindrance to Resonance.** When methyl groups in *tert*-butyl chloride or *p*-nitrobenzoates are replaced by *tert*-butyl and neopentyl groups, the reaction center of the molecule becomes more crowded and the rate of solvolysis increases. This phenomenon was explained in terms of rate-enhancing "B strain".[26] For example, Bartlett and co-workers reported that in the solvolysis of derivatives of highly hindered alcohols tri-*tert*-butylcarbinyl *p*-nitrobenzoate reacts 13 500 times faster than *tert*-butyl *p*-nitrobenzoate. Moreover, dineopentyl-*tert*-butylcarbinyl *p*-nitrobenzoate reacts 68 000 times faster.[27]

Recently the replacement of a methyl group by a *tert*-butyl group at the tertiary position of tertiary *p*-nitrobenzoates has been reported to result in rate enchancement by factors up to 1 120 000.[20]

Bulky groups at the reaction center of arylcarbinyl systems would similarly increase the B strain; however, since resonance between the developing p orbital of the carbonium ion and the $\pi$ orbitals of the aryl ring plays an important part in facilitating solvolysis of these systems, a rate-retarding tendency may result by twisting the developing p orbital of the cationic center out of conjugation with the aryl group. Indeed, steric inhibitation of resonance has been demonstrated in several investigations.[28]

**Table II. Rate Constants for the Solvolysis of *p*-Nitrobenzoates in 70% Acetone at 25.0 °C[a]**

| | $s^{-1}$ | | | |
|---|---|---|---|---|
| Group | 2-Propyl | *tert*-Butylneopentylcarbinyl | Dineopentylcarbinyl | Di-*tert*-butylcarbinyl |
| *p*-Anisyl | $1.34 \times 10^{-3}$ | $1.71 \times 10^{-4}$ | $8.48 \times 10^{-6}$ | $3.70 \times 10^{-8}$ |
| *p*-Tolyl | $9.73 \times 10^{-6}$ | $1.08 \times 10^{-6}$ | $2.00 \times 10^{-7}$ | $8.37 \times 10^{-9}$ |
| Phenyl | $4.58 \times 10^{-7}$ | $8.32 \times 10^{-8}$ | $6.21 \times 10^{-8}$ | $4.80 \times 10^{-9}$ |
| *p*-Chlorophenyl | $9.52 \times 10^{-8}$ | $2.31 \times 10^{-8}$ | $4.56 \times 10^{-9}$ | $1.40 \times 10^{-9}$ |
| *p*-Trifluoromethylphenyl | $5.39 \times 10^{-10}$ | $7.25 \times 10^{-10}$ | $3.82 \times 10^{-10}$ | $2.77 \times 10^{-10}$ |
| Methyl | $4.73 \times 10^{-10}$ [b] | $3.55 \times 10^{-7}$ | $1.15 \times 10^{-7}$ | $7.14 \times 10^{-8}$ |

[a] Calculated from rate constants at other temperatures from ref 28a unless otherwise noted. [b] Calculated by multiplying the rate constant in 80% acetone [H. C. Brown and W. C. Dickason, *J. Am. Chem. Soc.*, 91, 1226 (1969)] by the factor 1.68 (ref 8).

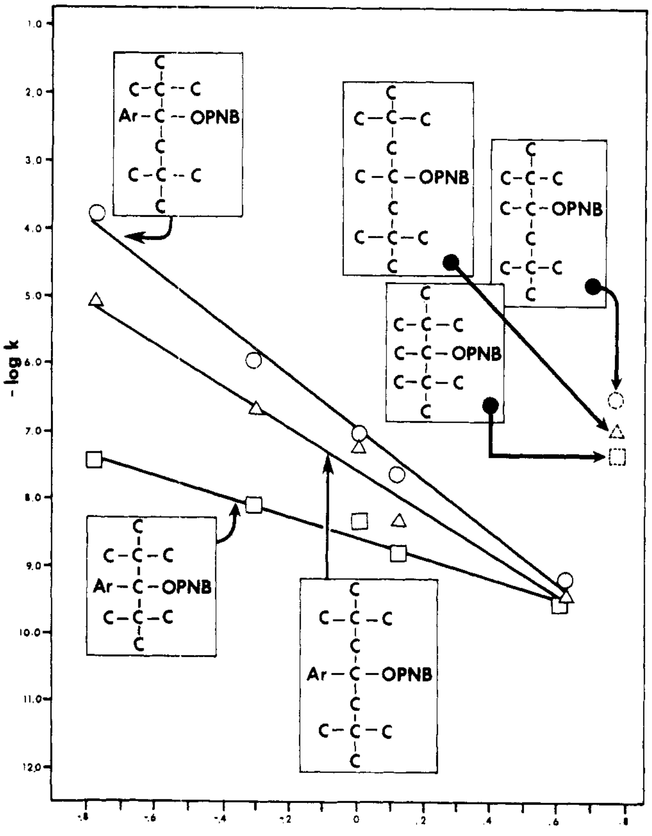


**Figure 1.** Nonlinearity in $\gamma^+$ vs. $-\log k$ plot of sterically hindered derivatives.

Tanida and Matsumura have studied a series of aryldialkylcarbinyl *p*-nitrobenzoates in which the alkyl groups varied from dimethyls to di-*tert*-butyl, dineopentyl, and *tert*-butylneopentyl.[28a] They observed a decrease in ρ values and attributed this to steric hindrance to resonance stabilization by the aryl group.

In order to fully explore the capabilities and limitations of correlating rates of solvolysis of tertiary methyl with tertiary benzylic derivatives, the effect of bulky groups was investigated.

Rate constants for aryl and methyl substituted 2-propyl, *tert*-butylneopentylcarbinyl, dineopentylcarbinyl, and di-*tert*-butylcarbinyl *p*-nitrobenzoates in 70% acetone at 25 °C are listed in Table II. For the aryl derivatives only, the ρ values are −4.60 (correlation coefficient 0.999), −3.87 (0.994), −3.14 (0.985), and −1.53 (0.984), respectively.

In the 2-propyl series, the 2-methyl derivative gives an excellent correlation with the 2-aryl derivatives. However, in the more bulky series nonlinear relationships are obtained. Figure 1 shows the $\rho\gamma^+$ plot for the aryl derivatives and an indication of the deviation of the methyl derivatives.

Clearly when steric hindrance to resonance is important, discretion must be employed in using the $\rho\gamma^+$ relationship in the correlation of nonaryl groups with aryl groups.

## Conclusion

A linear free energy relationship has been developed which permits the direct correlation of the rates of solvolysis of tertiary methyl derivatives with their corresponding tertiary benzylic derivatives.

This method was shown to be generally applicable to a large number of systems except in cases where the steric bulk at the cationic center results in steric hindrance to resonance stabilization.

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# A Method for the Evaluation of Steric Contributions to $\rho^+$ Based on Aryl/Methyl Rate Ratios. Application to the Gassman–Brown Tool of Increasing Electron Demand

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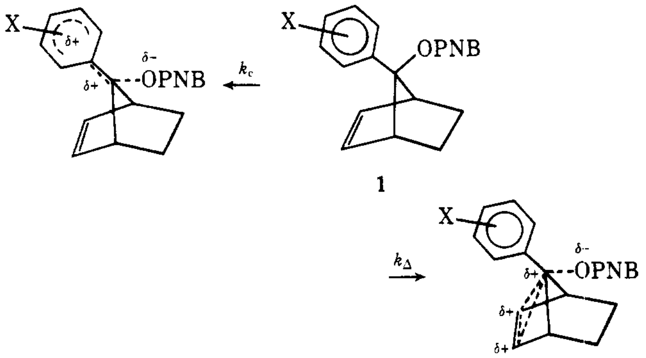
It has been shown that either of two factors may cause a large decrease in the magnitude of $\rho^+$ values determined for the solvolysis of a series of aryl-substituted tertiary derivatives. The factors are steric effects and neighboring group participation. In this article we define a method which can be empirically used to assess whether or not steric factors are affecting the magnitude of $\rho^+$. Toward this end a substituent constant, $\gamma^+$, for the methyl group directly attached to an incipient cationic center has been obtained by comparing *tert*-cumyl derivatives with *tert*-butyl derivatives. The constant is apparently solvent dependent with a value of 0.63 in 70–90% aqueous acetone and 0.79 in pure alcohols (methanol, ethanol, and 2-propanol). Using the derived $\gamma^+$ values, rate constants for methyl-substituted derivatives **6** were calculated. A comparison of calculated and observed rates for a variety of substrates reveals that the rates of **6** calculated from the rates of **7**, X = H, and $\rho^+$ are within 0.7 log units except when unusual steric effects cause a deviation. Both steric acceleration and steric deceleration of some aryl-substituted tertiary derivatives **7** were detected by the application of this treatment. The method described is applicable to both $k_c$ and $k_\Delta$ substrates.

Gassman and Fentiman[1] have observed that decreasing the electron demand at the reaction site in a substrate undergoing anchimerically assisted solvolysis can cause abrupt cessation in assistance by a neighboring group. Thus the *anti*-7-norbornenyl system (**1**) undergoes a change in mechanism from $k_\Delta$ to $k_c$ as the aryl group becomes sufficiently electron releasing to overcome the stabilization afforded by electron donation from the $C_2$–$C_3$ $\pi$ bond. This change in mechanism is reflected by the magnitude of $\rho^+$, which is −5.2 for hydrolysis of 1 in 70% aqueous dioxane when X = *p*-$NMe_2$ and *p*-OMe and −2.30 when X = H, *p*-$CF_3$, and *m,m'*-di-$CF_3$.



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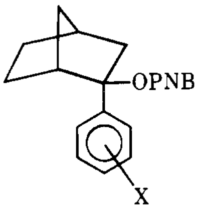
Brown and his co-workers[2–17] have made extensive use of the tool of increasing electron demand in characterizing a variety of systems. The method has been successfully used in detecting contributions from $\pi$ and $\sigma$ participation[1–15,17,18] and from other conjugating groups.[16] Yet examples where participation was not detected (e.g., the *exo*-2-norbornyl system, **2**)[2,11,18] or was too weak to positively identify (e.g., the *exo*-norbornen-2-yl system, **3**)[13,19] have also been treated.



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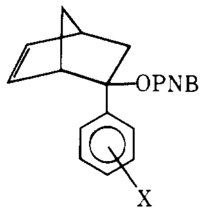

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Sargent[20] has claimed that the tertiary 2-norbornyl system (**2**) may undergo accelerated ionization because of relief of the nonbonded repulsion between the endo 6-H and the endo 2 substituent. Brown, however, has maintained[21] that his own data[22] and that of Goering and Schewene[23] show only a small difference (~0.4 kcal) between the ground-state free energies of the isomeric tertiary 2-norbornyl derivatives. Hence the tool of increasing electron demand is claimed to be valid for these systems since steric factors are similar in the exo and endo derivatives.[24] However, the fact that Brown and others have established that exo and endo tertiary 2-norbornyl derivatives have similar *ground state* energies does not rule out significant energy differences in the solvolytic *transition state*. Since the *preferred* ground state conformation and the *required* transition state conformations of aryl-substituted tertiaries may differ,[25] steric factors affecting the energy of the transition state are obviously the quantities which need assessing.

It is established that either steric factors[26] or neighboring group participation[1,7,10,17] can produce a remakable change in the magnitude of $\rho^+$. However, it has not been established whether or not these factors act independently or in concert in producing an effect on $\rho^+$, because previously there has been no method available to separate the effects of these factors. Accordingly, we have sought a method to evaluate the im-