Rates of Solvolysis of Substituted 4-Biphenylyldimethylcarbinyl Chlorides. A Test of the Free-energy Relationship

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The general applicability of Hammett Eq. 1 to the correlation of a large number, and a variety of, side-chain reactions and equilibria of aromatic derivatives is well established[1,2]. On the other hand, it has become progressively evident that electrophilic aromatic substitution reactions and some side-chain reactions, involving presumably stronger interactions between the substituent and the electron-deficient reaction center in the transition state do deviate from this equation[3,4].

$$\log k/k_0 = \rho\sigma \qquad (1)$$

Several sets of new substituent constants have thus been proposed by the workers[5-12] to reconcile their own results with the linear free-energy relationship of the type of Eq. 2.

$$\log k/k_0 = \rho\sigma^+ \qquad (2)$$

The fact that the new sets of substituent constants are more or less similar to each other might suggest that those reactions of the type which requires enhanced substituent constants constitute a distinct group on the one hand, as contrasted with the prevailing group of normal reactions on the other hand.

This view was encouraged by the considerable success in correlating a number of appropriate reaction rates by means of the modified substituent constants, σ^+, proposed by Brown and Okamoto[10-12]. There are a few cases of difficulties[13,14], however, which may likely escape the serious attention of proponents of the new treatments. Although the general success of σ^+ is apparent, it is still reasonable to state that the electronic contribution of a substituent could not be represented by a single constant as in Eq. 2, since the resonance contribution by a substituent can vary markedly from reaction to reaction, the very existence of different sets of substituent "constants" showing the non-reality of the "constants"[4,14,15].

In view of the utility of such equations over a wide variety of reactions it is not surprising that Eqs. 1 and 2 have been accepted with tolerance. This situation makes, however, proper evaluation of the linear free-energy relationship considerably complicated: in one case the deviation of a particular series of data may be attributed to a special interaction between the substituent and the solvent molecules or to anything which is convenient for rationalization of the result, in another case the deviation as detected may be thought to be due to experimental errors.

Therefore, it is desired to reexamine the linear free-energy relationship with due care, rather than to explore its utility. The study of the Hammett type relation should be done with the following things in mind; 1) Small deviations from the equation may be neglected in the first approximation. 2) Those deviations or agreements which are observed in the course of a study of a reaction of unknown or ambiguous mechanism do not argue against or for the validity of the relation. 3) The reaction series to be compared in relation to the equation should preferably be closely similar to each other so as to minimize unnecessary complications which may arise otherwise, although this would limit the virtue of the equation as far as its utilities are concerned.

Furthermore, it is anticipated that there will remain some uncertainty or arbitrariness in interpreting the results even if the study

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1) L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., New York, N. Y. (1940), Chapter 7.

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

3) J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, *J. Am. Chem. Soc.*, **76**, 4525 (1954).

4) P. B. D. de la Mare, *J. Chem. Soc.*, **1954**, 4450.

5) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

6) N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044, 3051 (1955).

7) C. W. McGary, Jr., Y. Okamoto and H. C. Brown, ibid., **77**, 3037 (1955).

8) J. Miller, *Aust. J. Chem.*, **9**, 61 (1956).

9) J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3445 (1953).

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

11) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

12) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

13) H. G. Kuivila and A. R. Hendrickson, ibid., **74**, 5068 (1952); H. G. Kuivila and C. E. Benjamin, ibid., **77**, 4834 (1955).

14) J. K. Kochi and G. S. Hammond, ibid., **75**, 3445 (1953); F. T. Fang, J. K. Kochi and G. S. Hammond, ibid., **80**, 563 (1958).

15) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution; Nitration and Halogenation", Butterworths Scientific Publications, London (1959), Chapter 18.

was made under ideal conditions. So far as we remain in the study of simple benzene derivatives, strictly following the original definition of the Hammett equation, such uncertainty always accompanies our interpretation since we have, at present, no basis of estimating how the resonance contribution of a substituent varies depending on the kind of reaction. Therefore it is desirable to find out an obvious case of deviation from the linearity by purposely providing selected conditions for a possible deviation.

In this paper we report the study on the rates of solvolysis of substituted 4-biphenylyldimethylcarbinyl chlorides in 90% acetone and compare them with that of substituted phenyldimethylcarbinyl chlorides[16)] under the identical conditions. It is reasonably hoped that the effects of various possible factors on the rate such as solvent interactions with the substituents and/or the reaction center are mostly compensated by comparison of the two series. The only difference is structural, i. e. the effect of the substituent in biphenyl derivatives is transmitted to the reaction center through the biphenyl ring system and that in benzene derivatives through the benzene ring. The two modes of transmission of the substituent effect, inductive and resonance, will play their roles in the biphenyl derivatives in a ratio different from that in the benzenes. Consequently, if these two series deviate from the linear relationship of free-energy of activation we will get an experimental foundation to believe that the deviations can be real and are understandable on the basis of the variance of the relative importance of the resonance and inductive contributions of the substituents.

Results

The substituted 4-biphenylyldimethylcarbinyl chlorides required were synthesized by treating the corresponding tertiary carbinols with dry hydrogen chloride in methylene chloride at 0°C and removing the solvent. Since the tertiary chlorides are unstable and difficult to purify, we were content with preparing pure samples of the tertiary carbinols and using the crude tertiary chloride directly, without further treatment[17)].

The tertiary chlorides were dissolved in 90% aqueous acetone and the first order rate constants of solvolysis determined at 0 and 25°C. Since the rates are to be compared with those of the substituted phenyldimethylcarbinyl chlorides by Brown and collaborators[16)], the water content of the solvent was adjusted to reproduce the original rate constant for phenyldimethylcarbinyl chloride. The rate constant for 4-biphenylyldimethylcarbinyl chloride was also reproduced quite well in this batch of solvent as it should be. Consequently there is no doubt about the identity of both the expermental conditions. Because of the fast rate exhibited by the 4′-methoxy compound, it was found difficult to obtain its precise rate constant at 25°C. Therefore, the more reliable value was calculated by using the thermodynamical quantities for activation obtained by

TABLE I. RATE CONSTANTS FOR THE SOLVOLYSIS OF THE ARYLDIMETHYLCARBINYL CHLORIDES IN 90% ACETONE

Aryl group	Rate constant, k_1(sec^{-1}) $\times 10^4$			Relative rate at 25°C
	0°C	15°C	25°C	
Phenyl	—	—	1.22	1.00
4-Biphenylyl	—	—	8.05^{a} (7.99 ; 8.12)	6.60
4′-MeO-4-biphenylyl	3.30^{b}	17.7^{a,b} (17.6 ; 17.8)	47.5^{a,b} (47.7 ; 47.4)	39.3
4′-Me-4-biphenylyl	1.01	—	16.8^{a} (16.8 ; 16.9)	13.8
4′-Cl-4-biphenylyl	—	—	4.39^{a} (4.43 ; 4.35)	3.60
4′-Br-4-blphenylyl	2.05	—	4.01^{a} (4.02 ; 3.99)	2.29
3′-Cl-4-biphenylyl	1.23	—	2.50^{a} (2.49 ; 2.50)	2.05

a) Mean of the data shown below in parentheses.

b) The least squares treatment of the data, in connection with Eyring equation, leads to 3.32, 17.4 and 48.0 at 0, 15 and 25°C, respectively, which will be adopted in further calculations.

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16) a) H. C. Brown and Collaborators, *J. Am. Chem. Soc.*, **79**, 1897, 1906, 1909 (1957); b) H. C. Brown, Y. Okamoto and T. Inukai, ibid., **80**, 4964 (1958).

17) This procedure has been verified by H. C. Brown et al. (Ref. 16a), and by the present author's experience using two samples of phenyldimethylcarbinyl chloride, one vacuum-distilled and one prepared by this procedure.

the least squares treatment of the observed rate constants at 0, 15 and 25°C. The agreement between the observed and the calculated figures was very satisfactory. The rate constants and the derived thermodynamic quantities of activation are presented in Tables I and II, respectively.

TABLE II. THERMODYNAMICAL QUANTITIES OF ACTIVATION FOR THE SOLVOLYSIS OF THE ARYLDIMETHYLCARBINYL CHLORIDES

Aryl group	$\Delta H^{\ddagger}$ kcal./mol.	$\Delta S^{\ddagger}$ e. u.
Phenyl	18.8[a]	−12.5[a]
4-Biphenylyl	18.0[a]	−12.2[a]
4′-MeO-4-biphenylyl	16.7	−13.0
4′-Me-4-biphenylyl	18.1	−10.5
4′-Cl-4-biphenylyl	—	—
4′-Br-4-biphenylyl	18.7	−11.5
3′-Cl-4-biphenylyl	18.9	−11.6

a) The value quoted from Ref. 16b

Discussion

The electrophilic subsituent constants, σ^+, for the substituted phenyl groups studied in this investigation, after the definition by Brown and Okamoto[10,12], are presented in Table III. They were calculated by the formula, $\log k/k_H = \rho\sigma^+$, where k_H is the rate constant for the solvolysis of phenyldimethylcarbinyl chloride in 90% acetone at 25°C and ρ is the reaction constant (−4.54)[12]. Hammett's σ values for these groups are also included in the table for ready comparison.

That the σ^+'s are consistently lower (more negative) than σ's is clearly due to the larger resonance contribution of the aryl groups in the solvolysis than the resonance contribution in the dissociation of benzoic acids (such tendency has been remarked in ortho-para directing groups already studied)[12].

TABLE III. SUBSTITUENT CONSTANTS FOR ARYL GROUPS

Group (para)	$\log k/k_H$	σ^+	σ[a]
C_6H_5-	0.819	−0.180	−0.0455
4-MeO-C_6H_4-	1.595	−0.351	−0.114
4-Me-C_6H_4-	1.14	−0.251	−0.0682
4-Cl-C_6H_4-	0.556	−0.122	+0.0985
4-Br-C_6H_4-	0.517	−0.114	+0.0985
3-Cl-C_6H_4-	0.312	−0.0686	(+0.0833)[b]

a) From the dissociation constants of substituted 4-biphenylcarboxylic acids in 50% (by volume) aqueous butyl cellosolve[18]

b) The value for 3-Br-C_6H_4-group (Ref. 18)

TABLE IV. RELATIVE RATE OF SOLVOLYSIS

X	Relative rate in X-C_6H_4-C_6H_4-CMe_2Cl	$\log k/k_H$	Relative rate in X-C_6H_4-CMe_2Cl	$\log k/k_H$
p-MeO	5.96	0.775	41700.	4.620
p-Me	2.09	0.320	26.0	1.415
H	1.00	0.000	1.00	0.000
p-Cl	0.545	−0.263	0.305	−0.516
p-Br	0.498	−0.303	0.208	−0.682
m-Cl	0.311	−0.508	0.0156	−1.807

In Table IV the effect of substituents on the rate of solvolysis of 4-biphenylyldimethylcarbinyl chlorides are compared with that found for the solvolysis of phenyldimethylcarbinyl chlorides[16]. Figure 1 shows the plot of $\log k/k_H$ for the solvolysis of 4-biphenylyldimethylcarbinyl chlorides versus σ^+, which is numerically equal to $-\log k/k_H \times 1/4.54$, as determined by using the data for the solvolysis of phenyldimethylcarbinyl chlorides.

It is clear in Fig. 1 that there is no simple relation between these two series of reactions. Since the size of the circles shown represents an experimental uncertainty of 3%, the "deviations" from a straight line, if any, are too large to be treated as experimental errors. Therefore, rather than draw a median line through these points, a line was drawn through H and *m*-Cl points in Fig. 1. Since the resonance contribution of the meta substituent is known to be negligible in the benzene series, it should be likewise negligible in biphenyl. This justifies the use of *m*-Cl point to fix an approximate reference line on which

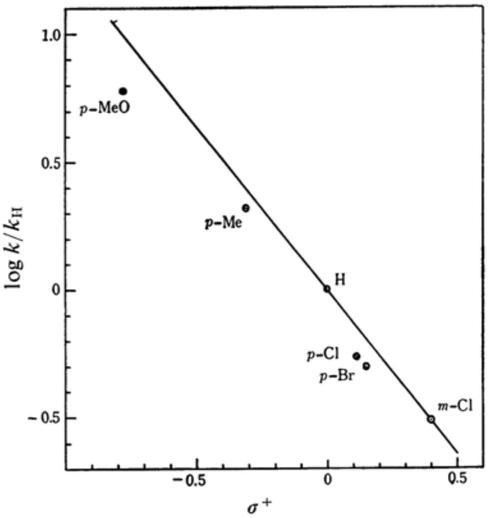

Fig. 1. Plot of $\log k/k_H$ for solvolysis of substituted 4-biphenylyldimethylcarbinyl chlorides versus σ^+.

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18) E. Berliner and L. H. Liu, *J. Am. Chem. Soc.*, **75**, 2417 (1953).

the para points would lie if the linear free-energy relationship held between these closely related reaction series. Thus the downward displacements from this line exhibited by the four para-substituted compounds correpond to the depression of the resonance contribution by these groups in biphenyl series, compared with the hypothetical resonance contributions expected from the linear free-energy relationship. The depression thus demonstrated agrees with the widely accepted view of the restricted conjugation through the pivot bond of biphenyl.

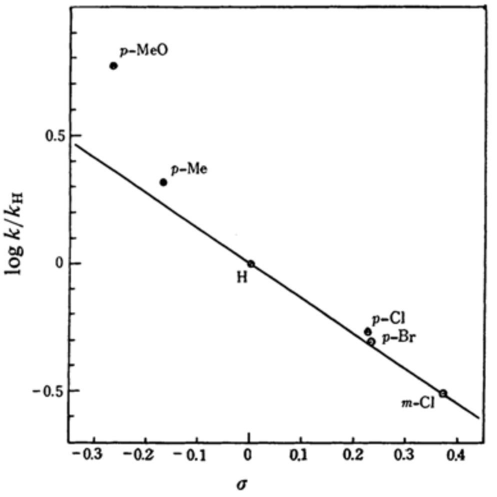


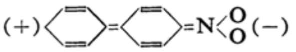
Fig. 2. Plot of $\log k/k_H$ for solvolysis of substituted 4-biphenylyldimethylcarbinyl chlorides versus Hammett's σ.

Figure 2 shows the plot of $\log k/k_H$ for biphenyl series versus the Hammett σ. The plot does not define any straight line either, but a straight line has been drawn through H and m-Cl points for the same purpose as above. This line approximately shows the hypothetical rates of reaction for biphenyl derivatives if the effect of the substituent on the rate were such that the linear free-energy relationship holds between the rates of the solvolysis of substituted biphenylyldimethylcarbinyl chlorides on the one hand and the equilibria of substituted benzoic acids on the other hand. The upward displacements of the points for the para substituted compounds from the line shown undoubtedly indicate the incorporation of additional resonance contribution in the solvolysis compared with that in the acid dissociation.

It is clear, from these discussions, that the features of the substituent effects in this solvolysis reactions are intermediate between those which characterize the solvolysis of phenyldimethylcarbinyl chlorides (σ^+-type) and dissociation of benzoic acids (σ-tye).

In searching for some criterion for the applicability of σ^+-values, the following view seems to be fundamentally correct. A resonance interaction or charge delocalization takes place powerfully between the substituent and the electron-deficient reaction center, in the transition state, a view which has been discussed by a number of workers[5-15] in this field and needs no elaboration.

On the basis of this view, the fact that the substituent effects in this solvolysis reactions are intermediate between σ^+-type and σ-type shows that the resonance interaction or charge delocalization which occurs in solvolysis of biphenylyldimethylcarbinyl chlorides is shared by the substituent in lesser degree than in the solvolysis of phenyldimethylcarbinyl chlorides. All chemical data can be explained satisfactorily on the basis of a restricted resonance of the two benzene rings in biphenyl. Thus the orientation in the electrophilic substitution of substiuted biphenyls conforms to the idea that the two rings act independently[19]. For example, Mizuno and Simamura[20] determined the partial rate factors for nitration of o-, m- and p-nitrobiphenyl with the results that the resonance formula like I, as would be reasonably suggested by simple application of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the electronic theory of organic reaction, is not a predominant factor in determining the reactivity of these compounds. A relative ineffectiveness of the substituent effect in the biphenyl system is also found in a nucleophilic displacement of 2, 4′-dinitro-4-bromobiphenyl[21]. From these chemical evidences it would be concluded that the resonance interactions extending over the biphenyl ring system is in general not influential in determining its chemical reactivities.

This situation only must be responsible for the break-down of the linear free-energy relationship, bipenyl derivatives versus phenyl derivatives, reported in this paper.

Consequently, the deviations from a linear free-energy relationship that have been observed in studies of benzene derivatives[13,14] can be ascribed, in some case and partly at least, to the variance of weight of the resonance contribution from reaction to reaction.

Modified Treatments.—Although the above arguments indicate that it is fundamentally

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[19] R. L. LeFevre and E. E. Turner, *J. Chem. Soc.*, **1928**, 245; For a discussion of this problem see also Ref. 18.

[20] Y. Mizuno and O. Simamura, *J. Chem. Soc*, **1958**, 3875.

[21] E. Berliner, B. Newman and T. M. Riaboff, *J. Am. Chem. Soc.*, **77**, 478 (1955).

TABLE V. SUBSTITUENT CONSTANTS

	σ^{a}	σ_I^{b}	$\sigma_R \equiv \sigma - \sigma_I$	σ^{+a}	$\Delta\sigma_R^{+} \equiv \sigma^{+} - \sigma$
H	0.000	0.000	0.000	0.000	0.000
4-MeO	−0.268	+0.23	−0.50	−0.778	−0.510
4-Me	−0.170	−0.05	−0.12	−0.311	−0.141
4-Cl	+0.227	+0.47	−0.24	+0.114	−0.113
4-Br	+0.232	+0.45	−0.22	+0.150	−0.082
3-Cl	+0.373	+0.47	−0.10	+0.399	+0.026

a) Ref. 12, b) Ref. 24

incorrect to assign a single substituent constant to a substituent, it may be still possible to correlate rates by means of a combination of two types of substituent constant, one for the inductive mode and the other for the resonance mode of electronic displacement. Such attempts have been made by Taft[22] (for shielding constants δ^F for fluorine NMR spectra of substituted fluorobenzenes), Corio and Dailey[23] (for proton NMR spectra of substituted benzenes) using σ_I and σ_R[24] and by Yukawa and Tsuno[26,27] for several reaction rate data proposing a formula, $\log k/k_H = \rho \cdot (\sigma + r\Delta\sigma_R^{+})$. The substituent constants used for the following computations are tabulated in Table V.

1) Taft's Treatment.—This method in effect treats the substituent effect as a composite of the inductive polar effect (σ_I) and the resonance polar effect (σ_R). Thus the actual formula is,

$$\log k/k_H = \alpha\sigma_I + \beta\sigma_R \qquad (3)$$

Least squares treatment of the present data by means of Eq. 3 leads to expression 4.

$$\log k/k_H = -2.282\sigma_I - 1.650\sigma_R - 0.014 \qquad (4)$$

The plot is shown in Fig. 3. Although this exhibits a satisfactory linearity, the apparent agreement does not prove that this procedure is a correct approach to reality since the introduction of one additional parameter affords a better opportunity of getting a better fit for no other reason but mathematical. The author believes that the success of this procedure suggests rather that the evaluation of σ_I and σ_R by Taft was fairly good.

2) Yukawa's Treatment. — Yukawa and Tsuno[25,26] recently proposed a modified Hammett type Eq. 5 for electrophilic reactions,

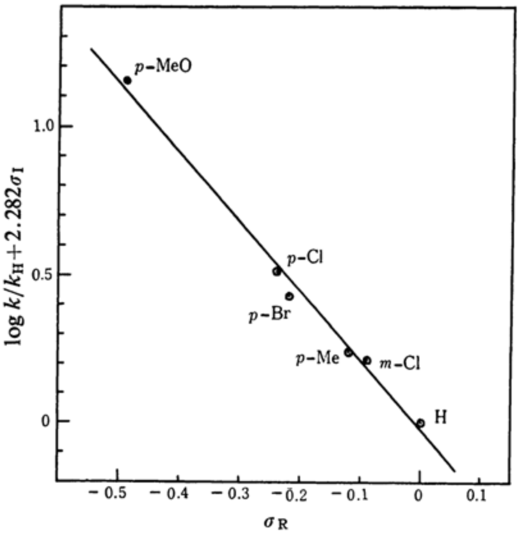

Fig. 3. Plot of $\log k/k_H + 2.282\sigma_I$ versus σ_R; Taft's treatment of the rates of solvolysis of substituted 4-biphenylyldimethylcarbinyl chlorides.

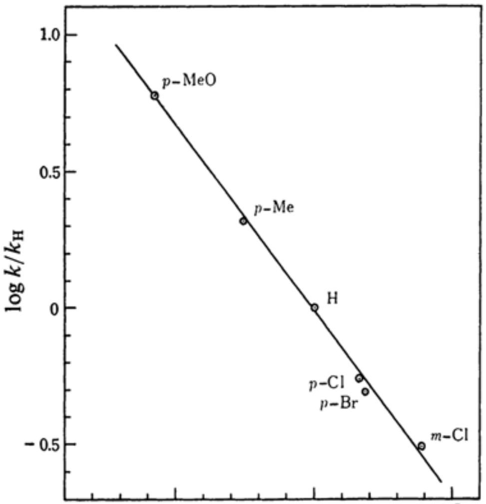

Fig. 4. Plot of $\log k/k_H$ versus $\sigma + 0.606\Delta\sigma_R^{+}$; Yukawa's treatment of the rates of solvolysis of substituted 4-biphenylyldimethylcarbinyl chlorides.

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[22] R. W. Taft, Jr., idid., 79, 1045 (1957).

[23] P. L. Corio and B. P. Dailey, ibid., 78, 3034 (1956).

[24] R. W. Taft, Jr., "Steric Effects in Organic Chemistry", John Wiley and Sons, Inc., New York (1956), Chapter 13.
σ_I, Inductive polar effect, σ_R, Resonance polar effect, $\sigma_R \equiv \sigma - \sigma_I$

[25] Y. Yukawa and Y. Tsuno, "Yuki Hanno Kiko no Shimpo", Vol. I., Maki Shoten, Tokyo (1958), Chapter 1.

[26] Y. Yukawa and Y. Tsuno, This Bulletin 32, 971 (1959).

[27] W. E. Bachmann and R. A. Hoffman, "Organic Reaction", Vol. II, John Wiley and Sons, Inc., New York (1944), p. 224.

$$\log k/k_{\mathrm{H}} = \rho(\sigma + r\Delta\sigma_{\mathrm{R}}{}^{+}) \qquad (5)$$

where r is a reaction constant describing the degree of resonance stabilization in the transition state, and $\Delta\sigma_{\mathrm{R}}{}^{+}$ is a substituent constant suggesting the resonating capacity of the substituent and is defined as $\Delta\sigma_{\mathrm{R}}{}^{+} \equiv \sigma^{+} - \sigma$. They demonstrated that Eq. 5 correlates the rate data more satisfactorily than Eq. 2 does, presenting the results of application of Eq. 5 to 35 different reactions. This method, applied to our present rate data, leads to Eq. 6.

$$\log k/k_{\mathrm{H}} = -1.363(\sigma + 0.606\Delta\sigma_{\mathrm{R}}{}^{+}) - 0.019 \quad (6)$$

The plot of $\log k/k_{\mathrm{H}}$ versus $\sigma + 0.606\Delta_{\mathrm{R}}{}^{+}$, Fig. 4, appears satisfactory.

3) *Limitations of Eq. 5.*—In view of the success of Eq. 5 in correlating a number of reaction series, it is interesting to see if it can successfully correlate the rates of solvolysis of the benzyl tosylates in 55.6 vol. % aqueous acetone at 25°C(14), which has given the greatest trouble to Brown-Okamoto's treatment(12) (Eq.2). The result of the least squares treatment of the rate data by means of Eq. 5 is expressed by Eq. 7 and has been shown in Fig. 5,

$$\log k/k_{\mathrm{H}} = -2.949\ (\sigma + 2.175\Delta\sigma_{\mathrm{R}}{}^{+}) + 0.057 \ (7)$$

The correlation thus obtained, Fig. 5, is no better than the σ^{+}-plot shown in Fig. 6. m-MeO and p-Cl compounds should react faster than the unsubstituted compound according to the correlation line in Fig. 5 or Eq. 7, which is of course contrary to the experimental observations. Such contradiction is also found in correlating the rate data of brominolysis of benzeneboronic acids(13) (see Fig. 9. of Ref. 27).

It is seen that although all the points have been brought closer to a straight line by introduction of a parameter, r, the m-MeO and p-Cl points thereby moved too far to the left-hand side (in Fig. 5). Consequently, it is difficult to take the r in Eq. 5 for a constant of reaction.

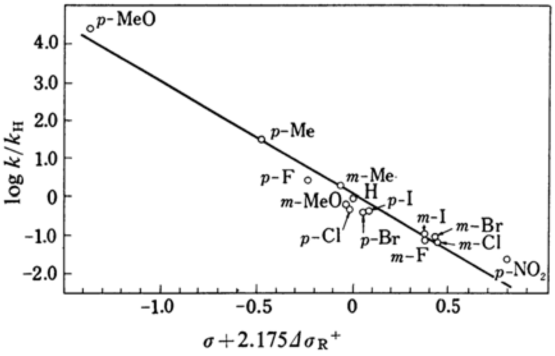

Fig. 5. Plot of $\log k/k_{\mathrm{H}}$ for solvolysis of the benzyl tosylates (Hammond's data) versus $\sigma + 2.175\Delta\sigma_{\mathrm{R}}{}^{+}$.

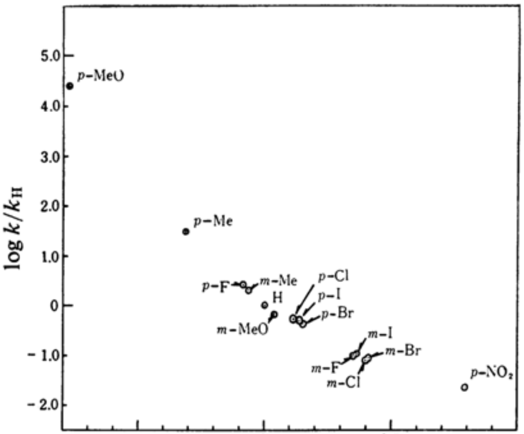

Fig. 6. Plot of $\log k/k_{\mathrm{H}}$ for solvolysis of the benzyl tosylates (Hammond's data) versus σ^{+}.

Experimental

The following monosubstituted biphenyls were prepared by the Gomberg-Bachmann reaction(27): p-Me, m. p. 48.5∼49.5°C (lit.(28) 47.7°C); p-Cl, m. p. 78.5∼79.5°C (lit.(29) 77.5°C); p-Br, m. p. 89.5∼90°C (lit.(30) 89.5∼90°C); m-Cl, b. p. 141∼143°/10 mmHg (lit.(31) 150∼160°C/6 mmHg). p-Methoxybiphenyl was prepared by methylation of commercial p-hydroxybiphenyl; m. p. 90∼91°C (lit.(32) 90°C).

All the 4-acetylbiphenyls used were prepared by the Friedel-Crafts acetylation of the corresponding biphenyls: 4′-H, m. p. 121∼122°C (lit.(33) 121°C); 4′-MeO, m. p. 153∼154°C (lit. 153∼154°C(34,35), 154.6∼155.5°C(36)); 4′-Me, m. p. 122∼123°C (lit.(37) 122°C); 4′-Cl, m. p. 102∼103°C (lit.(38) 102∼103°C); 4′-Br, m. p. 129°C (lit.(39) 131°C).

3′-Chloro-4-acetylbiphenyl.—To a mixture of m-chlorobiphenyl (22.5 g., 0.119 mol.), acetyl chloride (12 g., 0.153 mol.) and 100 ml. of dry carbon disulfide was added powdered anhydrous aluminum chloride (21 g., 0.158 mol.) in five portions over a

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34) W. S. Johnson, C. D. Gutsche and R. D. Offenhauer, ibid., **68**, 1648 (1946).

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37) N. P. Buu-Hoi, Ng. Hoan and R. Royer, *Bull. soc. chim.* France, (5) **17**, 489 (1951).

38) D. T. Mowry, M. Renoll and W. F. Huber, *J. Am. Chem. Soc.*, **68**, 1105 (1946).

39) B. R. Carpenter and E. E. Turner, *J. Chem. Soc.*, **1934**, 869.

TABLE VI. RATE DATA FOR THE SOLVOLYSIS OF 4-BIPHENYLYLDIMETHYLCARBINYL CHLORIDES AND PHENYLDIMETHYLCARBINYL CHLORIDE IN 90% ACETONE

1) 4-Biphenylyl-, 25°C

t, min.	a, ml.	k_1, min$^{-1}\times10^2$
0	0.498	—
2	1.185	4.753
4	1.800	4.715
6	2.385	4.774
9	3.167	4.826
12	3.842	4.852
15	4.403	4.830
∞	8.074	—
	Average	4.792

2) 4′-Methoxy-4-biphenylyl-, 0°C

t, min.	a, ml.	k_1, min$^{-1}\times10^2$
0	0.325	—
2	0.560	(2.052)
3	0.655	(1.937)
5	0.875	1.976
6	0.980	1.981
7.5	1.130	1.975
9	1.285	1.993
10.5	1.425	1.985
∞	6.171	—
	Average	1.982

3) 4′-Methoxy-4-biphenylyl-, 15°C

t, min.	a, ml.	k_1, min$^{-1}\times10$
0	0.592	—
1	1.080	1.075
2	1.516	1.072
3	1.902	1.065
4	2.254	1.066
∞	5.380	—
	Average	1.070

4) 4′-Methyl-4-biphenylyl-, 25°C

	t, min.	a, ml.	k_1, min$^{-1}\times10$
#1	0	0.500	—
	1	1.020	1.009
	2	1.490	1.009
	2.667	1.775	1.006
	∞	5.918	—
		Average	1.008
#2	0	0.398	—
	1	0.882	1.002
	2	1.330	1.015
	3	1.735	1.018
	∞	5.473	—
		Average	1.012

5) 4′-Chloro-4-biphenylyl-, 25°C

t, min.	a, ml.	k_1, min$^{-1}\times10^2$
0	0.305	—
5.1	1.300	2.568
9	1.965	2.546
12	2.485	2.611
14	2.810	2.641
16.25	3.185	2.702
18	3.325	2.590
20	3.595	2.604
∞	8.410	—
	Average	2.609

6) 4′-Bromo-4-biphenylyl-, 0°C

t, min.	a, ml.	k_1, min$^{-1}\times10^3$
0	0.048	—
65	0.330	1.234
214	0.895	1.230
312	1.212	1.227
341	1.305	1.234
344	1.310	1.230
430	1.554	1.233
∞	3.707	—
	Average	1.231

7) 4′-Bromo-4-biphenylyl, 25°C

t, min.	a, ml.	k_1, min$^{-1}\times10^2$
0	0.160	—
4	0.350	2.325
7	0.485	2.353
13	0.730	2.382
16	0.847	2.420
20.6	0.998	2.412
24	1.110	2.445
28	1.212	2.416
∞	2.300	—
	Average	2.393

8) 3′-Chloro-4-biphenylyl-, 0°C

t, min.	a, ml.	k_1, min$^{-1}\times10^4$
0	0.080	—
103	0.635	7.207
241	1.355	7.450
291	1.600	7.493
355	1.882	7.446
372	1.952	7.423
377	1.980	7.451
∞	7.838	—
	Average	7.412

TABLE VI (Continued)

9) 3′-Chloro-4-biphenylyl-, 25°C

t, min.	a, ml.	k_1, min$^{-1}\times10^2$
0	0.315	—
10	1.080	1.487
14	1.347	1.473
18	1.625	1.500
22	1.870	1.498
26	2.110	1.507
30	2.334	1.512
34	2.532	1.495
∞	5.852	—
	Average	1.496

10) Phenyl-, 25°C

t, min.	a, ml.	k_1, min$^{-1}\times10^3$
0	0.820	—
13	1.595	7.297
21	2.040	7.320
34	2.710	7.335
42	3.090	7.334
54	3.625	7.350
61	3.950	7.459
∞	9.383	—
	Average	7.349

period of 20 min. without external heating. The mixture was stirred for 10 min. longer and was refluxed for 1/2 hr. Cooled in an iced water bath the complex was decomposed with dilute hydrochloric acid. The carbon disulfide was removed by distillation and the residue recrystallized twice from ethanol; yield 10 g. (36%). Colorless needles, m. p. 57.5∼58.5°C. (Found: C, 73.09; H, 4.73. Calcd. for $C_{14}H_{11}OCl$: C, 72.89, H, 4.81%). This material was a sole isolable product from the reaction above. The position of the acetylation is most probably 4′ by analogy with the similar acetylation of 3-bromobiphenyl[36].

All the 4-biphenylyldimethylcarbinols used were prepared by the action of methylmagnesium iodide on the corresponding ketones: 4′-H, m. p. 91.5∼92.5°C (lit. 92∼93°C[40], 91.5∼92.5°C[16b]); 4′-MeO, m. p. 137∼137.5°C, recrystallized from benzene (Found: C, 79.39; H, 7.31. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%); 4′-Me, m. p. 116∼116.5°C, recrystallized from benzene (Found: C, 84.89; H, 8.09. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02%); 4′-Cl, m. p. 143.2∼144.2°C, recrystallized from benzene (Found: C, 73.16; H, 6.29; Cl, 14.36. Calcd. for $C_{15}H_{15}OCl$: C, 73.02; H, 6.13, Cl, 14.37%); 4′-Br, m. p. 143∼145°C, recrystallized from benzene (Found: C, 61.61; H, 5.21; Br, 27.47. Calcd. for $C_{15}H_{15}OBr$: C, 61.87; H, 5.19; Br, 27.45%); 3′-Cl, m. p. 74∼75°C, recrystallized from petroleum ether (Found: C, 73.20; H, 6.14; Cl, 14.36. Calcd. for $C_{15}H_{15}OCl$; C, 73.02; H, 6.13; Cl, 14.37%).

Kinetic Measurement.—The solvent, 100 ml., was placed in a long-necked flask and brought to reaction temperature. Approximately 1 g. of the tertiary chloride was dissolved in the solvent and 5 ml. aliquots were removed at appropriate intervals of time. The aliquots were run into 100 ml. of ice-cold dry acetone to stop the reaction and hydrogen chloride was titrated with 0.03 N sodium ethoxide/ethanol using a solution of 3 parts of bromocresol green and 1 part of methyl red in ethanol as an indicator. The reaction mixture was allowed to stand overnight to obtain the aliquots for the "infinity" titer. The first-order rate constants, k_1, were calculated by the formula, $k_1=[\ln(a_\infty-a_0)-\ln(a_\infty-a_t)]/t$, where a_0, a_t and a_∞ stand for the titer at time 0, t and "infinity", respectively.

Some of the rate data for the solvolysis of 4-biphenylyldimethylcarbinyl chlorides and phenyldimethylcarbinyl chloride in 90% acetone are presented in Table VI.

Summary

The rates of solvolysis of 4′-MeO-, 4′-Me-, 4′-H-, 4′-Cl-, 4′-Br- and 3′-Cl-4-biphenylyldimethylcarbinyl chlorides in 90% aqueous acetone have been determined and compared with those of the correspondingly substituted phenyldimethylcarbinyl chlorides. The effect of substituents is very much depressed in biphenyl derivatives as compared with that in phenyl derivatives, and a remarkable deviation from the linear free-enegy relationship was observed between these systems. This is attributed to the difference in the relative importance of the resonance effect and inductive effect of substituents between these two different systems.

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