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A METHOD FOR ASSESSING ELECTROPHILIC SUBSTITUENT EFFECTS IN THE GAS-PHASE, AND THE CORRELATION WITH REACTIVITY IN THE CONDENSED-PHASE*

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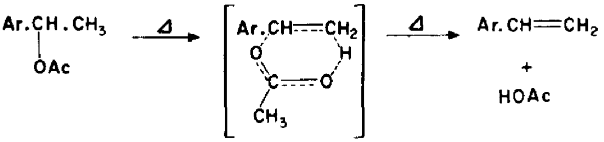
Abstract—Substituent effects in the gas-phase pyrolysis of 1-arylethyl acetates (a reaction which proceeds *via* a transition state of carbonium ion character) are compared with those obtained in condensed-phase electrophilic aromatic substitutions and related reactions, and are found to closely parallel them. The *p*-methyl and *p*-t-butyl substituents activate in the inductive order, disproving the contention that the Baker–Nathan effect is primarily a function of the resonance requirement of a particular reaction. It is shown that the variable reactivity of the *para*-position in biphenyl in electrophilic and related reactions is unlikely to be attributable to an energy barrier restricting the attainment of a coplanar form, and that the electrophilic reactivity of the 2-position in fluorene cannot be satisfactorily represented by a single substituent constant. Sigma values in reactions proceeding via electron deficient centres are revealed as being partially dependent upon the extent of solvation though this effect is relatively minor. The pyrolysis reaction promises to be of fundamental value for examining the effects of substituents known to be strongly susceptible to solvent effects in condensed-phase reactions. Steric effects in the reaction are discussed.

INTRODUCTION

HOMOGENEOUS gas-phase reactions provide the ideal systems for studying the effect of structural changes on the rate of chemical reactions since solvent influences are eliminated. We have recently demonstrated[1] that the pyrolysis of 1-arylethyl acetates to olefins and acetic acid proceeds via a carbonium ionic mechanism since it follows precisely a $\rho\sigma^+$-correlation (Brown and Okamoto[2]); the reaction is therefore allied to electrophilic aromatic substitutions and related reactions which also proceed via the formation of an electron deficient centre but have been carried out in the condensed phase.



Brown *et al.*[3] have been very successful in relating the effects of substituents in the solvolysis of t-cumyl chlorides to those in a number of reactions which also proceed *via* electron-deficient transition states. This has led to the introduction of σ^+-values

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* Studies in Pyrolysis, Part VI.

[1] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, **84**, 4817 (1962).

[2] H. C. Brown and Y. Okamoto, *Ibid.*, **80**, 4979 (1958).

[3] For a summary of this work, see H. C. Brown and L. M. Stock. *Ibid.*, **84**, 3298 (1962).

to describe, semiquantitatively, these substituent effects, and although not true constants, they appear to be as successful as the Hammett σ- "constants" in their appropriate applications[4]. Thus while the solvolysis reaction has been of indisputable value, it suffers from the disadvantage of being a condensed-phase reaction, and further, isolation of the pure t-cumyl chlorides is difficult or impossible. The pyrolysis reaction does not have these disadvantages and therefore promises to be a useful measure of substituent effects in electrophilic and related reactions. This paper describes some resonance, polar, and steric effects revealed from a comparison of substituent effects in this reaction with those in related condensed-phase reactions.

TABLE 1. RELATIVE RATES OF PYROLYSIS OF 1-ARYLETHYL ACETATES
X in $XC_6H_4CH.OAc.CH_3$

X	log $k_{rel.}$	X	log $k_{rel.}$	X	log $k_{rel.}$	X	log $k_{rel.}$
p-MeO	0·500	*o*-Me	0·215	*p*-F	0·035	*p*-Br	−0·110
3,4-C_7H_6[a]	0·395	*p*-Me	0·190	H	0·000	*m*-F	−0·230
o-MeO	0·260	2,3-C_4H_4[b]	0·140	*m*-Ph	0·000	*m*-Cl	−0·245
o-Ph	0·235	*p*-Ph	0·140	*p*-Cl	−0·070	*m*-F	−0·245
p-t-Bu	0·220	3,4-C_4H_4[c]	0·115	*p*-I	−0·080	*m*-NO_2	−0·420

[a] 2-fluorenyl [b] α-naphthyl [c] β-naphthyl

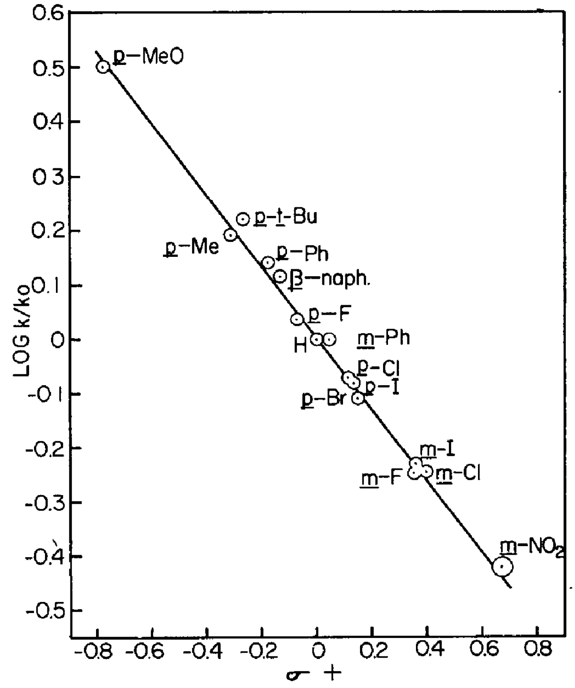

FIG. 1.

The experimental details have previously been given and the kinetic data are summarized in Table 1; Fig. 1 gives the plot of the log k/k_0 (log k_{rel}) values *vs.* σ^+-values ($\rho = -0{\cdot}66$). This plot differs from that which we previously gave[1] in one

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[4] L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, **81**, 3323 (1959); **84**, 1668 (1962).

important respect. We formally used the value of $\sigma^{+}_{m-\mathrm{Ph}}$ (+ 0·109) given by Brown and Okamoto[2] and the point for the *m*-phenyl substituent deviated considerably from the linear plot. The value has since been reassessed by Stock and Brown[5] as +0·05 ± 0·01 and with this value Fig. 1 shows improved linearity.

DISCUSSION

Solvent effect on sigma values

Ritchie and Lewis have recently summarized the reasons why sigma values may exhibit solvent dependence[6]. These are (i) the direct interaction between the substituent and the reaction site may be influenced by the solvent, (ii) a specific interaction may occur between the solvent and the substituent, (iii) there may be a general breakdown of Hammett-type relationships such that σ-values are reaction dependent. From a study of the relative acidities of bicyclooctane acids in various media [the possibility of (i) occurring being thus eliminated] Ritchie and Lewis concluded that since anomalous results were obtained in dimethyl sulphoxide, either (ii) or (iii) might be real. If sigma values are solvent dependent then maximum deviations should be observed by comparing values determined in the gas-phase with those determined in solution. A detailed examination of individual substituent effects will show if (ii) occurs, whilst (iii) should be detectable as a general trend for a whole range of substituents in any given reaction. This latter point will be considered first.

The application of a specific set of σ^+-constants to electrophilic aromatic substitutions (and related reactions) has been considered unsatisfactory since the amount of resonance stabilization of the positive reaction centre in each reaction will be different,[7] and various more-quantitative treatments of substituent effects have been proposed[7j,k,8]. The treatment of Yukawa and Tsuno appears sound in conception and successful in application.[8–11] The factor r in their equation *viz.* $\log k/k_0 = \rho[\sigma + r(\sigma^+ - \sigma)]$ is a measure of the resonance interaction between the substituents and the reaction centre in any given reaction. Yukawa and Tsuno have shown that r varies from reaction to reaction but not linearly with ρ although the latter is a measure of the extent of charge formation in the transition state. One reason for this may be that the reactions considered have positive centres developing both in the aromatic ring

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[5] L. M. Stock and H. C. Brown, *Ibid.*, **84**, 1242 (1962).

[6] C. D. Ritchie and E. S. Lewis, *Ibid.*, **84**, 591 (1962).

[7a] P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954).

[b] D. E. Pearson, J. P. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

[c] J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, *J. Amer. Chem. Soc.*, **76**, 4525 (1954).

[d] J. K. Kochi and G. S. Hammond, *Ibid.*, **75**, 3445 (1953); G. S. Hammond *et al.*, *Ibid.*, **80**, 563, 568, 573 (1958).

[e] N. C. Deno and A. Schriesheim, *Ibid.*, **77**, 3051 (1955).

[f] N. C. Deno and W. L. Evans, *Ibid.*, **79**, 5804 (1957).

[g] J. Miller, *Aust. J. Chem.*, **9**, 61 (1956).

[h] Y. Tsuno, T. Ibata and Y. Yukawa, *Bull. Chem. Soc. Japan*, **32**, 960, 965 (1959).

[i] Y. Ogata and I. Tabushi, *J. Amer. Chem. Soc.*, **83**, 3440, 3444 (1961).

[j] H. Van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. Trav. chim.*, **78**, 815 (1959).

[k] J. R. Knowles, R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).

[8] Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 971 (1959).

[9] C. Eaborn and R. Taylor, *J. Chem. Soc.*, 1012 (1961).

[10] C. Eaborn and J. A. Waters, *Ibid.*, 542 (1961).

[11] C. Eaborn and K. C. Pande, *Ibid.*, 5082 (1961).

and in the side chain. We believe that the non-linearity of r and ρ may be partly the result of solvent influences, since the extent to which solvation may help to stabilize the electron-deficient transition state is unlikely to be constant from reaction to reaction. The following fact suggests that this is of particular importance. Application of the Yukawa and Tsuno treatment to our data gives a value of $r \simeq 1$ whereas ρ is only $-0{\cdot}66$. The value of r is very large relative to ρ (compared with r and ρ values obtained in solution reactions) and this arises because there is no opportunity for solvent stabilization of the transition state in our reaction. In solution reactions, solvation will help to stabilize the positive charge either at the reaction site or elsewhere in the aromatic ring or side-chain so that the amount of electron release required from the substituents (and measured by r) will be reduced. Hence r will be smaller relative to ρ than for a gas-phase reaction where solvation cannot occur. Thus since electrophilic substituent values are variable according to the demand for resonance stabilization of the electron deficient centre, and since the demand will be partly satiated by solvation, then the values will not be entirely independent of the media in which the reaction is carried out.

Individual substituent effects in the pyrolysis reaction should be explainable in terms of the Yukawa and Tsuno equation, and any deviations may reasonably be attributed to the absence of solvent. Substituent effects in the pyrolysis and condensed-phase reactions are compared below in order to reveal any such deviations. In conjunction with the condensed-phase data, the pyrolysis reaction reveals further information on the electronic effects operating in the aromatic molecule.

The halogen substituents. The Yukawa and Tsuno equation predicts that for a condensed-phase reaction of r-value ca. 1·0, the p-fluoro substituent should activate relative to hydrogen, and the other *para*-halogens should give the relative reactivity order $Cl > I > Br$. This is precisely the result observed in the pyrolysis reaction, so that individual halogens are not apparently susceptible to solvent effects.

Biphenyl, naphthalene, and fluorine substituents. The ratio of the reactivity of the *para*-position in biphenyl to that of the *beta*-position in naphthalene ($\log f_p^{\mathrm{Ph}}/\log f_{3,4}^{\mathrm{C_4H_4}}$ can vary widely in condensed-phase reactions. For example, in protodegermylation[12] it is 1·70 and in detritiation[9] it is 0·96. For a condensed-phase reaction of r-value ca. 1·0, a value of 1·33 is predicted and the pyrolysis reaction gives $1{\cdot}22 \pm 0{\cdot}1$ so that the reactivities of these positions are not specially affected by solvent effects in the condensed-phase.

In the pyrolysis reaction the 2-position in fluorine is more reactive than the *para*-position in biphenyl as expected[13], the ratio $\log f_{3,4}^{\mathrm{C_7H_6}}/\log f_p^{\mathrm{Ph}}$ being 2·82. Eaborn *et al.* have shown[9,14] that the reactivity of the p-phenyl group cannot be satisfactorily represented by a σ^+-constant, since a linear correlation between $\log f_p^{\mathrm{Me}}$ and $\log f_p^{\mathrm{Ph}}$ does not exist. Stock and Brown attribute this[5] to an energy barrier restricting the attainment of the coplanar form required for the release of electrons by resonance in the transition state. In reactions of increased selectivity, the steric forces are considered to be increasingly overcome by the greater energy requirements of the transition state thus giving variable activation by the p-phenyl substituent. Thus they argue that

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[12] C. Eaborn and K. C. Pande, *Ibid.*, 297 (1961).

[13] P. D. B. de la Mare and J. H. Ridd, "Aromatic Substitution, Nitration, and Halogenation", Butterworth's Scientific Publications, London, 1959, p. 158.

[14] F. B. Deans, C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 3031 (1959).

the *p*-phenyl substituent is a special case and the plot of $\log f_p^{\mathrm{Me}}$ *vs.* $\log f_{3,4}^{\mathrm{C_7H_6}}$ (which we believe to be curved) is linear, showing that "the 2-position of fluorene conforms to the Selectivity Relationship over a wide range of reagent reactivity". The fact that a correlation between $\log f_p^{\mathrm{Me}}$ and $\log f_{3,4}^{\mathrm{C_4H_4}}$ is also non-linear[9] was unfortunately neglected; the variable reactivity of the *beta*-position in naphthalene clearly cannot be a steric effect.

Fluorene has an enforced coplanar structure and hence mesomeric electron release reduces the activation energy for reaction at the 2-position making this position more reactive than the *para*-position in biphenyl. (The activation energy is also reduced to a small extent by the electron releasing properties of the bridging methylene group). It is our belief that the reactivity of the 2-fluorenyl position will nevertheless be enhanced by electromeric stabilization of the transition state. Consider the data in Table 2, where the reactions are arranged in increasing order of *r*-value. If the reactivity at the 2-position of fluorene is at a constant maximum, as Brown and Stock suggest, then the $\log f_{3,4}^{\mathrm{C_7H_6}}/\log f_p^{\mathrm{Ph}}$ value should decrease *regularly* with increasing *r*-value. This is not observed. The ratio is initially high due to the mesomeric effect enhancing the reactivity of the 2-position of fluorene. As the demand for the electromeric effect increases, biphenyl will increasingly attain a planar configuration and opportunities for electromeric stabilization of the *para*-position will be greater; the ratio will fall. However, in reactions of large resonance requirements the ratio becomes constant. This provides strong evidence that the reactivity of the 2-position of fluorene becomes also enhanced by the electromeric effect, and cannot be satisfactorily represented by a single substituent constant.

TABLE 2

Reaction	$\log f_{3,4}^{\mathrm{C_7H_6}\,a}/\log f_p^{\mathrm{Ph}}$	Ref.
Protodesilylation	3·00	15
Mercuration	2·63	16
Ester pyrolysis	2·82	this work
Solvolysis	2·74	17
Detritation	1·91	18
Acetylation	1·89	19
Molecular chlorination	1·97	5,20
Molecular bromination	1·97	21

[a] 2-fluorenyl

Finally, this study demonstrates that there is no detectable difference in the reactivity of biphenyl in the gas-, and condensed-phases. For example, in the pyrolysis

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[15] C. Eaborn, *Ibid.*, 4858 (1956), and personal communication.
[16] H. C. Brown, M. Dubeck and G. Goldman, *J. Amer. Chem. Soc.*, **84**, 1229 (1962).
[17a] Y. Okamoto, T. Inukai and H. C. Brown, *Ibid.*, **80**, 4972 (1958).
[b] H. C. Brown and T. Inukai, *Ibid.*, **83**, 4825 (1961).
[18] R. Baker and C. Eaborn, personal communication.
[19] H. C. Brown and G. Marino, *J. Amer. Chem. Soc.*, **84**, 1236 (1962).
[20a] P. B. D. de la Mare, D. M. Hall, M. M. Harris and M. Hassan, *Chem. & Ind.* (*Rev*) 1086 (1958).
[b] S. F. Mason, *J. Chem. Soc.*, 1233 (1959).
[21] H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, **84**, 1238 (1962).

reaction the *p*-phenyl substituent shows no deviation on the plot against σ^+-values. This result can logically be interpreted as follows: *Either* the angle between the phenyl rings must be the same in both phases *or* the suggestion of Stock and Brown, namely that the variable reactivity of the *para*-position in biphenyl arises because the energy barrier restricts attainment of the coplanar configuration, is untenable. In the gas-phase the angle between the phenyl rings has been found[22] to be 45°, whereas in solution, values between 0 and 20° have been suggested.[23] The evidence at present available indicates that the latter interpretation is the less likely.

The *meta*-phenyl substituent has the same reactivity as hydrogen in the pyrolysis reaction, whereas for a condensed-phase reaction of *r*-value ca. 1·0 a small deactivation should be obtained. However, there are insufficient grounds at present for attributing the lower (and rather variable) reactivity in condensed-phase reactions to solvent effects. Firstly there is considerable doubt[5] as to the correct σ^+-value for this substituent. Secondly the partial rate factors in many condensed-phase reactions are determined by compution methods in which the percentage of *meta* product is very small and difficult to assess accurately. Thirdly, the limitation of the present pyrolysis apparatus is such that we would be unable to detect a very small deactivation in this reaction of very small ρ-value.

The methyl and t-butyl substituents. From our results a $\log f_p^{\text{t-Bu}}/\log f_p^{\text{Me}}$ value of 1·16 is obtained whereas for a condensed-phase reaction of *r*-value ca. 1·0 a value of 0·82 is predicted. Because there is a marked difference in these values it seems very probable that the reactivity of either, or both, of the substituents is influenced by the solvent in condensed-phase reactions. Inductive activation orders have been obtained in only four condensed-phase reactions with electron-deficient transition states. These are nitration in acetic acid containing 10% of water[24] (1·06), detritiation in trifluoroacetic acid–aqueous sulphuric acid[25] (1·04) and trifluoroacetic acid–aqueous perchloric acid[25] (1·03), mercuridesilylation[26] (1·12), and protodestannylation[10] (1·14). [Knowles *et al.* obtained a value of 1·05 for nitration by fuming nitric acid in glacial acetic acid[7k].]

It has been suggested that hyperconjugative electron release plays a minor role in determining the reactivity of methyl substituted and related compounds[7k]. It was argued that reactions having very small ρ-factors have a small demand for resonance in the transition state. The relative reaction rates would here be governed by the ground state electrons densities, as measured by the σ-constants for the substituents. Benkeser *et al.*[26] also considered that this might be a plausible view. Thus in reactions which have small ρ-factors an inductive activation order would be expected, and since our reaction has the smallest *f*-factor so far observed for reactions proceeding *via* electron deficient centres, then the $\log f_p^{\text{t-Bu}}/\log f_p^{\text{Me}}$ value should be the largest observed, as indeed it is. However, in nitration[24] an inductive order results ($f_p^{\text{Me}} = 58$, $f_p^{\text{t-Bu}} = 75$), yet in positive bromination[27] the Baker–Nathan order is obtained ($f_p^{\text{Me}} = 59$, $f_p^{\text{t-Bu}} = 38{\cdot}5$) although the electron demand of the attacking species is similar

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[22] O. Bastiensen, *Acta Chem. Scand.*, **3**, 408 (1949); **4**, 926 (1950); **6**, 205 (1952); O. Bastiensen and L. Smedvik, *Ibid.*, **9**, 1593 (1954).

[23] J. Y. Chan, C. G. LeFevre and R. J. W. LeFevre, *J. Chem. Soc.*, 2666 (1959).

[24] H. Cohn, E. D. Hughes, M. H. Jones and M. G. Peeling, *Nature, Lond.* **169**, 291 (1952).

[25] C. Eaborn and R. Taylor, *J. Chem. Soc.*, 2417 (1961).

[26] R. A. Benkeser, T. V. Liston and G. M. Stanton, *Tetrahedron Letters*, **15**, 1 (1960).

[27] P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, 36 (1956); 131 (1957).

to that in nitration. In detritiation in aqueous sulphuric acid, where the f_p^{Me} value of 250 determines the activity of the attacking species, the Baker–Nathan order applies, yet in detritiation in trifluoroacetic acid–aqueous perchloric acid where $f_p^{\mathrm{Me}} = 313$, the inductive order applies.[25] The ρ-factor for a reaction is therefore clearly not a satisfactory indication of the relative activation orders of the *p*-Me and *p*-t-Bu groups. Neither can the overall resonance demand in a reaction be the factor controlling the relative activation order, for our reaction has the same demand as the solvolysis of t-cumyl chlorides, yet the relative activation order is the reverse. It is therefore our opinion that the concept of solvent enhancement of carbon–hydrogen hyperconjugation over carbon–carbon hyperconjugation in some media provides, at present, the most satisfactory explanation of the Baker–Nathan effect. This is supported by the work of Shiner and Verbanic,[28] by the detritiation result that the inductive order is obtained in the least polar medium, by the fact that the inductive order in mercuridesilylation[26] is obtained in a less polar medium than that used for protodesilylation[15] (which gives the Baker–Nathan order), and by the present work, which, being carried out in the absence of a solvent, gives the inductive order.

Steric effects in the reaction

Steric effects in the pyrolysis reaction are compared, below, with those obtained in condensed-phase reactions to ascertain the limitations imposed by the bulky nature of the side-chain. The origins of some steric effects in condensed-phase reactions are revealed.

The methyl substituent. Norman and Radda have analysed the $\log f_o^{\mathrm{Me}}/\log f_p^{\mathrm{Me}}$ ratios for a number of electrophilic aromatic substitution reactions and have found that the ratio decreases as the configuration of the transition state (indicated by ρ) more nearly resembles the Wheland intermediate.[29] Baker *et al.* have also shown that for detritiation in various media, the ratio decreases as the ρ-factor increases.[30] It is possible that the Norman and Radda treatment is applicable to side-chain reactions, so that a fully charged carbonium ion in the transition state would be analogous to the Wheland intermediate. The solvolysis of t-cumyl chlorides has a fully charged carbonium ion in the transition state, yet the ρ-factor is only $-4{\cdot}6$ which indicates that removing the positive charge to the α-carbon atom reduces the ρ-factor approximately threefold. Our reaction would therefore correspond to an aromatic substitution of ca. 2·0 for which the Norman and Radda treatment predicts the $\log f_o^{\mathrm{Me}}/\log f_p^{\mathrm{Me}}$ value of ca. 1·1 i.e. very close to the observed value of 1·13. The reactivity of the *o*-methyl ester does not seem therefore to be sterically affected.

The methoxy substituent. Our reaction gives a $\log f_o^{\mathrm{MeO}}/\log f_p^{\mathrm{MeO}}$ value of 0·52, but analysis of this result is difficult owing to the paucity of other data. In aromatic substitution, the combination of the greater deactivation of the *ortho*-position by the —I effect, and the preferential relay of the +E effect to the *para*-position should give a decreasing ratio as the resonance demand increases. The available data *viz.* degermylation[31] (0·837), desilylation[15] (0·795), dedeuteration[32] (0·92) and molecular

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[28] V. J. Shiner, *J. Amer. Chem. Soc.*, **76**, 1603 (1954); *Tetrahedron*, **5**, 243 (1959). V. J. Shiner and C. J. Verbanic, *J. Amer. Chem. Soc.*, **79**, 369 (1957).

[29] R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 3610 (1961).

[30] R. Baker, C. Eaborn and R. Taylor, *Ibid.*, 4927 (1961).

[31] C. Eaborn and K. C. Pande, *Ibid.*, 297 (1961).

[32] D. P. N. Satchell, *Ibid.*, 3911 (1956).

bromination[33] (0·805) does not indicate this; the demetalation reactions may be affected by steric acceleration, while the dedeuteration may be affected by hydrogen bonding.[34] Comparison of our result with that for molecular bromination suggests that the reactivity of the *o*-methoxy ester is reduced by steric hindrance—examination of molecular models indicates that the bulky nature of the side-chain in the transition state prevents the *ortho*-methoxy group from attaining the configuration required for maximum resonance with the aromatic ring.

The naphthyl substituent. The $\log f^{C_4H_4}_{2,3}/\log f^{C_4H_4}_{3,4}$ value (the relative reactivities of the α- and β-positions in naphthalene) for the pyrolysis reaction is 1·22. No complete analysis of the reactivities of these positions in other reactions has previously been made. It is first necessary to do this in order to assess the origin and magnitude of steric effects operating in reactions at the α-position. The available data is therefore collected in Table 3 where the reactions are (approximately) in order of increasing *r*-value. The data for the arylcarbinyl chloride solvolyses will not be discussed because the reaction mechanism may not have been the same throughout; in the aqueous formic acid medium the reaction rate for the unsubstituted compound was uncertain.

There is a wide variation in the $\log f^{C_4H_4}_{2,3}/\log f^{C_4H_4}_{3,4}$ ratios which can be explained by the concept of steric hindrance and/or acceleration for reaction at the α-position. Assume that the ratio of 1·4–1·6 in hydrogen exchange (where steric effects are small[30]) is that which we should attain for a linear free-energy relationship between the reactivities of the α- and β-positions. The results for nitration, bromination, and

TABLE 3

Reaction	$\log f^{C_4H_4}_{2,3}/\log f^{C_4H_4}_{3,4}$	Ref.
Protodegermylation	3·14	31
Protodesilylation	2·72	35
Bromodesilylation	2·09	35
Nitration	1·58	36
Ester pyrolysis	1·22	This work
Solvolysis $ArCMe_2Cl$ in aq. acetone	1·02	37
Solvolysis $ArCMe_2Cl$ in aq. ethanol	0·75	38
Solvolysis $ArCHMeCl$ in aq. acetone	1·43	37
Solvolysis $ArCH_2Cl$ in aq. formic acid/dioxan	2·62	39
Solvolysis $ArCH_2Cl$ in aq. formic acid	1·91	38
Detritiation in $CF_3COOH—H_2O—HClO_4$	1·43	9
Detritiation in CF_3COOH	1·40	34
Detritiation in $CF_3COOH—H_2O—H_2SO_4$	1·44	9
Molecular bromination (xs. bromide ion)	1·56	40
Dedeuteration in liquid HBr	1·54 ~ 1·59	41

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[33] P. B. D. de la Mare and C. A. Vernon, *Ibid.*, 1764 (1951).

[34] C. Eaborn. Presonal communication.

[35] C. Eaborn, Z. Lasocki and D. E. Webster, *J. Chem. Soc.*, 3034 (1959).

[36] M. J. S. Dewar, T. Mole and E. W. T. Warford, *Ibid.*, 3573, 3576, 3581 (1956).

[37] Y. Okamoto and H. C. Brown, *J. Amer. Chem. Soc.*, **79**, 1903 (1957).

[38] M. J. S. Dewar and R. J. Samson, *J. Chem. Soc.*, 2789 (1956); 2946, 2952 (1957).

[39] P. J. C. Fierens, H. Hannaert, J. Van Ryselberge and R. H. Martin, *Helv. Chim. Acta*, **38**, 2009 (1955).

[40] E. Berliner and J. C. Powers, *J. Amer. Chem. Soc.*, **83**, 905 (1961).

[41a] E. N. Yurigina, P. P. Alikhanov, E. A. Izrailevich, P. N. Manochkina and A. I. Shatenshtein, *Zhur. Fiz. Khim.*, **34**, 587 (1960).

[b] A. I. Shatenshtein and P. P. Alikhanov, *Zhur. Obschei. Khim.*, **30**, 992 (1960).

solvolysis of arylmethylcarbinyl chlorides then appear accounted for. Although Dewar and Samson showed[38] that arylcarbinyl chlorides with a "1-naphthalene" type of structure solvolysed at reduced rates due to steric interaction between the *peri-* and side-chain hydrogens, it does not necessarily follow that the solvolyses of arylmethylcarbinyl chlorides (with a bulkier side-chain) would be similarly affected since the reaction medium was quite different. Steric effects of this type however do occur in the solvolysis of aryldimethylcarbinyl chlorides in aqueous acetone where a much lower ration is obtained;[37] this ratio is even smaller if the solvolysis is carried out in aqueous ethanol[38] presumably because there is also steric hindrance to the entering ethoxy group.

Eaborn *et al.*[31,35] have attributed the high ratios in protodesilylation and protodegermylation to relief (through attaining a more tetrahedral configuration in the transition state) of the steric strain which exists between the *peri*-hydrogen and the α-substituent. In suppport of this concept we note that this steric acceleration is more marked for removal of the bulkier triethylgermanyl group. Eaborn *et al.*[35] suggested that the value for bromodesilylation represents a balance of steric acceleration and steric hindrance to the incoming (moleculear) bromine. The more recent data for molecular bromination appears, at first, to contradict this. However, the configuration of the bonds will be less sp^3 in bromodesilylation than in molecular bromination because the reactivity of the attacking species (as indicated by the ρ-factor) is greater in the former reaction. Steric hindrance to the incoming bromine, though absent in molecular bromination, will therefore almost certainly be finite in bromodesilylation as the results suggest.

Thus the ratio in the pyrolysis reaction is lower than expected for the existence of a linear free-energy relationship between the reactivities of the α- and β-positions, and it is reasonable to attribute this to steric hindrance at the α-position. In the transition state of the pyrolysis reaction the incipient cyclic side-chain will tend to become coplanar with the naphthyl ring. For the α-isomer this tendency will be restrained by steric interactions with the *peri*-hydrogen and opportunities for resonance stabilization of the carbonium ionic centre will be reduced.

The phenyl substituent. The $\log f_o^{\mathrm{Ph}}/\log f_p^{\mathrm{Ph}}$ value for the pyrolysis reaction is 1·68. A very recent accumulation of experimental data enables us to make the most complete analysis yet of the relative reactivities of the *ortho-* and *para*-positions in biphenyl. All of the known data is gathered in Table 4 where the reactions are (approximately) in order of increasing r-value. The large variation in the $\log f_o^{\mathrm{Ph}}/\log f_p^{\mathrm{Ph}}$ ratio is doubtless mainly of steric origin since there is no regular variation with r-value. Before deciding upon the origin of these steric effects it is necessary to determine what ratio could be expected in the absence of them.

Localization energy[36,45] and other[45b,46] calculations predict that the reactivity of

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[42] O. Simamura and Y. Mizuno, *Bull. Chem. Soc. Japan*, **30**, 196 (1957); *J. Chem. Soc.*, 3875 (1958).

[43] C. J. Billing and R. O. C. Norman, *Ibid.*, 3885 (1961).

[44] P. B. D. de la Mare and M. Hassan, *Ibid.*, 3004 (1957).

[45a] M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3337, 3341 (1952).

[b] F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Farad. Soc.*, **47**, 553 (1951).

[c] S. F. Mason, *J. Chem. Soc.*, 1233 (1959).

[d] R. D. Brown, *Experientia*, **6**, 376 (1950); *J. Amer. Chem. Soc.*, **75**, 4077 (1953).

[46] Von G. Dallinga, A. A. Verrijn Stuart, P. J. Smit and E. L. Mackor, *Z. Electrochem*, **61**, 1010 (1957).

the *ortho*-position should be equal to, or rather greater than, that of the *para*-position, a prediction apparently justified by the data for detritiation, since primary steric effects are unimportant in this reaction.[30] Thus one may assume that steric hindrance in nitration (the data of Dewar appears to be in error), positive bromination, and molecular chlorination is small, and becomes increasingly greater in molecular bromination, ethylation, and mercuration—the existence of a steric effect for mercuration was indicated by an enhanced entropy of activation for *ortho*-substitution.

TABLE 4

Reaction	$\log f_o^{Ph}/\log f_p^{Ph}$	Ref.
Ethylation	−0·12	5
Protodestannylation	1·20	10
Protodegermylation	1·18	31
Protodesilylation	1·74	14
Mercuridesilylation	0·77	14
Mercuration (25°)	−0·13	5
Bromodesilylation	0·094	14
Nitration	1·22	36
Nitration	1·02	42
Nitration	1·03	43
Ester pyrolysis	1·68	This work
Detritiation in $CF_3COOH—H_2O—HClO_4$	0·985	9
Detritiation in $CF_3COOH—H_2O—H_2SO_4$	1·000	9
Bromination by Br^+ (or $BrOH_2^+$)	0·86	44
Molecular chlorination	0·91	20(*a*)
Molecular bromination	0·45	5

For reactions involving the replacement of groups other than hydrogen, a satisfactory explanation of the results, compatible with that advanced to account for the relative reactivities of the α- and β-positions of naphthalene, is now possible. It is first assumed that for any given reaction, the transition state for *ortho*-substitution in biphenyl is more crowded than for α-substitution in naphthalene. This assumption is supported by examination of molecular models, and comparison of the depression of the $\log f_o^{Ph}/\log f_p^{Ph}$ ratio with the absence of any affect on the $\log f_{2,3}^{C_4H_4}/\log f_{3,4}^{C_4H_4}$ ratio in the molecular bromination of biphenyl and naphthalene, respectively. It therefore follows that not only will steric hindrance be greater for reaction at the *ortho*-biphenyl position than at the α-naphthyl position, but that steric acceleration will be smaller. Steric acceleration arises here from relief, in the transition state, of the steric strain between the substituent and the *ortho*-hydrogen of the other ring.[14]

The experimental results confirm the above assumptions. Steric acceleration for protodesilylation of the *ortho*-biphenyl position is less than it was for the α-naphthyl position. The balance, in bromodesilylation, of steric hindrance and steric acceleration which was weighted in favour of acceleration for naphthalene, is weighted in favour of hindrance for biphenyl.* For the α-position of naphthalene, steric acceleration was greater for protodegermylation than for protodesilylation but for the *ortho*-position in biphenyl, steric acceleration is less for protodegermylation and protodestannylation than for protodesilylation. This anomaly can however be explained, for it is reasonable to assume that the more crowded *ortho*-biphenyl transition state does not permit sufficient relief of steric strain when very bulky groups are present. Also, since the degermylation and destannylation reactions are less selective than the desilylation, the disposition of the bonds at the reaction position will be less tetrahedral in the transition state so that less opportunity for relief of steric strain will be afforded.

The result for mercuridesilylation provides an interesting demonstration of the balancing of steric hindrance and acceleration. The selectivities of the mercuration, proto-, and mercuri-desilylation reactions are very similar. The configuration of the bonds in the transition states of each reaction will also be similar. The value of $\log f_o^{Ph}/\log f_p^{Ph}$ in mercuridesilylation could therefore be expected to be the average of the values obtained in the other two reactions. The data in Table 4 shows that this is indeed the case, the expected value of 0·80 being very close to the observed value of 0·77.

From the above discussion it seems probable that the $\log f_o^{Ph}/\log f_p^{Ph}$ value for ester pyrolysis is not only high, but that it can be explained in terms of steric acceleration. The bulky side-chain forces the phenyl group further out of coplanarity than in biphenyl itself and since the reaction product has only a vinyl group in the *ortho*-position, there is thus considerable relief of steric strain in going through the transition state.

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* It is noted that the small steric hindrance in molecular bromination has become much larger in bromodesilylation, in keeping with the view that steric interactions are least in reactions having the most tetrahedral configuration of bonds at the carbon atom at which substitution occurs.[14] Weingarten, on the contrary, has suggested that steric hindrance is *greatest* in the transition state of reactions of *highest* selectivity.[47] This postulate was based upon the fact that a f_o^{Ph}/f_p^{Ph} *vs.* f_m^{Ph}/f_p^{Ph} plot for chlorination of biphenyl under various conditions showed a sharp fall-off in the former value as the latter tended to zero. However, if a linear free-energy relationship exists (even approximately) between the reactivities of the three positions in biphenyl so that $\log f_o^{Ph}/\log f_p^{Ph}$ and $\log f_m^{Ph}/\log f_p^{Ph}$ are both constants, and if the former value is slightly less than unity and the latter value is small, as seems reasonable for biphenyl, then a plot of f_o^{Ph}/f_p^{Ph} *vs.* f_m^{Ph}/f_p^{Ph} *should*, being of exponential form, exhibit a sharp decrease in the former ratio as the latter tends to zero. Further, the former ratio should tend towards unity as the latter becomes large. Since these trends were those experimentally observed, we are unable to accept the steric concepts proposed by Weingarten.

[47] H. Weingarten, *J. Org. Chem.* **26**, 4347 (1961).