

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

An Examination of the Applicability of the Selectivity Relationship to the Electrophilic Substitution Reactions of *t*-Butylbenzene¹⁻³BY LEON M. STOCK^{4,5} AND HERBERT C. BROWN

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The available data for the electrophilic substitution reactions of *t*-butylbenzene have been examined by conventional statistical procedures for adherence to the Selectivity Relationship and related equations. The least squares analysis indicated a more than satisfactory correlation of the experimental results. The ratio, $\log p_{t\text{-Bu}}/\log m_{t\text{-Bu}}$, is 2.89 ± 0.49 for eleven reactions. The average percentage error in the reaction constant is 8.64% compared to 3.64% for the corresponding substitution reactions of toluene. Examination of the results reveals that the principal cause of this larger deviation is a direct consequence of uncertainty in the influence of the *m*-*t*-butyl substituent. The σ -constants for the electrophilic substitution of *t*-butylbenzene are $\sigma_{m\text{-}t\text{-Bu}}^+ = -0.090$ and $\sigma_{p\text{-}t\text{-Bu}}^+ = -0.260$. The former value is somewhat larger than the σ_m^+ constant for *t*-Bu, -0.059 , based upon the *t*-cumyl chloride solvolysis data. On the other hand, the σ_p^+ constant is in excellent agreement with the value, -0.256 , derived from the solvolysis results.

The suggestion that the electrophilic substitution reactions of toluene⁶⁻⁸ and other monosubstituted benzenes^{6,7} were governed by a linear relationship was first made in 1953. In the intervening years experimental results have been obtained for 47 substitution reactions of toluene. The excellent correlations demonstrated for these 47 reactions indicated that the Selectivity Relationship⁸ was obeyed with more than satisfactory precision for the methyl substituent.⁹ In addition, the adherence of these substitution data to the relationship was clearly superior to the correlations achieved with the available results for electrophilic side-chain or normal Hammett side-chain reactivities for this substituent.⁹

In concurrent studies, it has been observed that many electrophilic side-chain reactions were satisfactorily correlated through the application of σ^+ constants based on the relative rates of solvolysis of substituted *t*-cumyl chlorides.^{10,11} The observations for electrophilic substitution reactions of the monosubstituted benzenes also appear to be compatible with these constants.¹² These encouraging results have prompted further investigations concerning the merit of a general relationship^{6,7} governing electrophilic substitution reactions.

It often has been predicted that a relation of this type would not apply to aromatic substitution reactions. These arguments have been based on the concept that resonance contributions to the stabilization of the transition state would vary greatly with the reactivity of the reagent.¹³⁻¹⁵ In view of this argument and the preliminary indications of the general nature of the relationship, a more compre-

hensive examination of other substituent groups appeared desirable. Moreover, a study of the reactions of activated monosubstituted benzenes should offer an excellent test of the possible extension of the relationship. A program was therefore initiated to examine the electrophilic reactivity of *t*-butylbenzene, biphenyl and anisole.¹⁶

An examination of the literature revealed that six substitution reactions of *t*-butylbenzene had been studied quantitatively.¹⁷ Since these results were largely for reactions of intermediate reagent activity, it was desirable to obtain additional results for reagents of widely different selectivity. Accordingly, the non-selective mercuration¹⁸ and the selective Friedel-Crafts acylation¹⁹ and non-catalytic halogenation²⁰ were studied. The observations of these studies and the previous results provide the basis for a test of the applicability of the Selectivity Relationship to *t*-butylbenzene.

Summary of Available Results and Statistical Evaluation.—The partial rate factors and associated quantities for the electrophilic substitution reactions of *t*-butylbenzene are summarized in Table I. For convenient comparison, the data for the corresponding reactions of toluene are included. In our examination of the application of the Selectivity Relationship to the data for substitution in toluene, it was desirable to separate the substitution reactions into two series on the basis of their apparent experimental validity.⁹ For substitution in *t*-butylbenzene, the partial rate factors are based on approximations in only two cases. The *para* partial rate factor for Friedel-Crafts benzylation in nitrobenzene²¹ (entry 6) depends on an assumed quantitative yield of *p*-*t*-butylbenzophenone. This assumption appears fully justified on the basis of recent chromatographic analyses of the reaction products in the benzylation of *t*-butylbenzene in ethylene chloride solution.¹⁹ The m_t value for the deuterium exchange reaction of *t*-butylbenzene²²

(1) Directive Effects in Aromatic Substitution. XLI.

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(3) Based upon a thesis submitted by Leon M. Stock in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) Monsanto Chemical Co. Fellow, 1957-1958.

(5) Department of Chemistry, University of Chicago.

(6) H. C. Brown and K. L. Nelson, *THIS JOURNAL*, **75**, 6292 (1953).(7) H. C. Brown and C. W. McGary, *ibid.*, **77**, 2300 (1955).(8) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).(9) L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).(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, *THIS JOURNAL*, **80**, 4979 (1958).(13) P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954).(14) J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, *THIS JOURNAL*, **76**, 4525 (1954).(15) V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 2743 (1956).

(16) The results for the other substituent groups will be reported subsequently.

(17) We are indebted to W. M. Lauer, C. Eaborn and R. A. Benkeser for generously informing us of their observations prior to publication.

(18) H. C. Brown and M. Dubeck, *THIS JOURNAL*, **81**, 5608 (1959).(19) H. C. Brown and G. Marino, *ibid.*, **81**, 5611 (1959).(20) L. M. Stock and H. C. Brown, *ibid.*, **81**, 5615 (1959).(21) H. C. Brown, B. A. Bolto and F. R. Jensen, *J. Org. Chem.*, **23**, 414 (1958).(22) W. M. Lauer, G. W. Matson and G. Stedman, *THIS JOURNAL*, **80**, 6433, 6437 (1958); W. M. Lauer and G. Stedman, *ibid.*, **80**, 6439 (1958).

TABLE I
 SUMMARY OF PARTIAL RATE FACTORS AND ASSOCIATED QUANTITIES FOR TOLUENE AND *t*-BUTYL BENZENE

| No. | Reaction, conditions ^a | Toluene | | | | $\frac{\log p_i}{\log m_i}$ | <i>t</i> -Butylbenzene | | | $\frac{\log p_i}{\log m_i}$ | Ref. |
|-----|--|---------------|----------|----------|-------|-----------------------------|------------------------|------------|------------|-----------------------------|------|
| | | σ^{Me} | m^{Me} | p^{Me} | S | | σ^{t-Bu} | m^{t-Bu} | p^{t-Bu} | | |
| 1 | Bromination, Br ₂ , 85% HOAc, 25° | 600 | 5.5 | 2420 | 2.644 | 4.57 | 4.97 | 6.09 | 806 | 3.71 | 20 |
| 2 | Chlorination, Cl ₂ , HOAc, 25° | 617 | 4.95 | 820 | 2.219 | 4.19 | 56.6 | 6.0 | 401 | 3.33 | 20 |
| 3 | Chlorode- <i>t</i> -butylation, ArC(CH ₃) ₃ , Cl ₂ , HOAc, 25° | | | 610 | | | | | 380 | | 20 |
| 4 | Acetylation, CH ₃ COCl, AlCl ₃ , C ₂ H ₅ Cl ₂ , 25° | 4.5 | 4.8 | 749 | 2.192 | 4.22 | 0.0 | 13.1 | 658 | 2.53 | 19 |
| 5 | Benzoylation, C ₆ H ₅ COCl, AlCl ₃ , C ₂ H ₄ Cl ₂ , 25° | 29.4 | 4.9 | 633 | 2.107 | 4.06 | 0.0 | 11.4 | 398 | 2.46 | 19 |
| 6 | Benzoylation, C ₆ H ₅ COCl, AlCl ₃ , C ₆ H ₅ NO ₂ , 25° ^b | 32.5 | 5.0 | 830 | 2.221 | 4.18 | | | 615 | | 21 |
| 7 | Deuteration, D ₂ O, CF ₂ CO ₂ H, 70° ^c | 253 | 3.8 | 421 | 2.046 | 4.52 | 198 | 7.0 | 490 | 3.18 | 22 |
| 8 | Nitration, HNO ₃ , 90% HOAc, 45° | 42 | 2.5 | 58 | 1.366 | 4.43 | 5.5 | 4.0 | 75 | 3.12 | 24 |
| 9 | Bromination, HOBr, HClO ₄ , 50% dioxane, 25° | 76 | 2.5 | 50 | 1.373 | 4.45 | 13.7 | 2.60 | 38.6 | 3.82 | 25 |
| 10 | Desilylation, ArSiMe ₃ , Br ₂ , HOAc, 25° | | 3.2 | 49 | 1.185 | 3.35 | | | 29 | | 26 |
| 11 | Desilylation, ArSiMe ₃ , HClO ₄ , 50% MeOH, 51° | | 2.3 | 21.2 | 0.963 | 3.66 | | | 15.6 | | 27 |
| 12 | Desilylation, ArSiMe ₃ , HCl, HOAc, 25° ^d | | 2.14 | 20.1 | .973 | 3.95 | | 2.98 | 11.9 | 2.27 | 28 |
| 13 | Mercuration, Hg(OAc) ₂ , HOAc, 50° | 4.60 | 1.98 | 16.8 | .928 | 4.12 | 0.0 | 3.04 | 15.6 | 2.44 | 18 |
| 14 | Mercuration, Hg(OAc) ₂ , HOAc, 70° | 4.03 | 1.83 | 13.5 | .867 | 4.30 | 0.0 | 2.66 | 10.8 | 2.45 | 18 |
| 15 | Mercuration, Hg(OAc) ₂ , HOAc, 90° | 3.51 | 1.70 | 11.2 | .819 | 4.56 | 0.0 | 2.58 | 9.61 | 2.44 | 18 |

^a The electrophilic reagent is presented first, followed by the catalyst, solvent and temperature. ^b The value for p_i^{t-Bu} is based on an assumed isomer distribution. ^c The value for m_i^{t-Bu} is based on rate data for *p*-di-*t*-butylbenzene. ^d Conditions glacial acetic acid, 1.17 *M* HCl, 3.62 *M* H₂O. These conditions are slightly different from those employed by Benkeser and his associates as reported in ref. 28.

(entry 7) was estimated from the measured rate of exchange of *p*-di-*t*-butylbenzene and a knowledge of the *ortho* partial rate factor for the reaction. This procedure frequently has been employed to obtain an estimate or a confirmatory result for an experimental isomer distribution with good precision.²³ In all other cases, spectroscopic, isotopic dilution or gas phase chromatographic procedures have been utilized to determine the isomer distributions. The necessary relative rate measurements and kinetic partial rate factors are the result of apparently reliable techniques. Thus, a separation of these results into two groups, such as that utilized in analyzing the toluene data,⁹ was not considered necessary.

In the earlier evaluation of the relationship for toluene,⁹ the corresponding correlation of electrophilic and normal Hammett side-chain reactivities were contrasted with the results for the electrophilic substitution reactions. Unfortunately, data for the *t*-butyl substituent in reactions of this type are not widely available. Although several reactions of the *p*-*t*-butyl substituent have been studied, only a limited amount of information is available for the *meta* isomer. Even more rarely are data available for both the *meta* and *para* isomers under the same conditions. Under these circumstances,

(23) See for example, H. C. Brown and L. M. Stock, *THIS JOURNAL*, **79**, 1421, 5175 (1957), and ref. 20.

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

(25) P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, 131 (1957).

(26) C. Eaborn and D. E. Webster, *ibid.*, 4449 (1957).

(27) R. A. Benkeser and R. A. Hickner, unpublished results.

(28) See also R. A. Benkeser, R. A. Hickner and D. I. Hoke, *THIS JOURNAL*, **80**, 2279 (1958).

several of the critical evaluations cannot be employed. Consequently, these reaction types will not be examined here.

In the conventional application of the Hammett equation

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

the constancy of the σ -parameters is assumed. In order to test the applicability of the equation to the reaction under consideration, the quantity $\log(k/k_0)$ is plotted against σ . The reaction constant, ρ , then is evaluated from the slope of the line.

In the attempted extension of this equation to electrophilic reactions, the constancy of the σ^+ -values cannot be assumed. To test this question, the linear dependence of $\log(k/k_0)$ on ρ^+ could be examined to test the invariant nature of σ^+ for the substituent in question. The slope of the line would then give σ^+ . To avoid frequent changes in its value, the reaction constant ρ should be based upon substitution data for a number of substituents of different types. Unfortunately, such data are not yet available.

It is seen readily that $\log m_i$ and $\log(p_i/m_i)$ are proportional to the reaction constant.²⁹ Consequently, these quantities may be adopted instead of the reaction constant itself. This is the essence of the Selectivity Treatment. Applied to the methyl substituent in the form of the three equations (1-3),²⁹ it clearly established the essential constancy of the σ^+ -value for the methyl substituent.⁹

$$\log p_i = \frac{\sigma_p^+}{\sigma_m^+} \log m_i \quad (1)$$

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

$$\log p_i = \frac{\sigma_p^+}{\sigma_p^+ - \sigma_m^+} \log (p_i/m_i) \quad (2)$$

$$\log m_i = \frac{\sigma_m^+}{\sigma_p^+ - \sigma_m^+} \log (p_i/m_i) \quad (3)$$

These equations can be utilized directly for testing the constancy of the σ^+ -value for the *t*-butyl and other substituents.

In utilizing the equation in this form, partial rate factors are required for substitution both in the *meta* and *para* positions. In the case of many substituents, such as methoxy, substitution occurs predominantly in one position so that this procedure is not easily applicable. Of course, when ρ values are available, this difficulty will no longer exist. Meanwhile, it appears desirable to utilize $\log (p_i^{\text{Me}}/m_i^{\text{Me}}) = S_i$ as a quantity proportional to ρ to test the applicability of the Selectivity Treatment to other substituents of interest. Since both $\log p_i^{\text{Me}}$ and $\log m_i^{\text{Me}}$ are also proportional to ρ , these quantities can also be utilized in this way.

In this way we arrive at the expressions 4-7.

$$\log p_i^{t\text{-Bu}} = \frac{\sigma_{p-t\text{-Bu}}^+}{\sigma_{p-\text{Me}}^+ - \sigma_{m-\text{Me}}^+} \log (p_i^{\text{Me}}/m_i^{\text{Me}}) \quad (4)$$

$$\log m_i^{t\text{-Bu}} = \frac{\sigma_{m-t\text{-Bu}}^+}{\sigma_{p-\text{Me}}^+ - \sigma_{m-\text{Me}}^+} \log (p_i^{\text{Me}}/m_i^{\text{Me}}) \quad (5)$$

$$\log p_i^{t\text{-Bu}} = \frac{\sigma_{p-t\text{-Bu}}^+}{\sigma_{p-\text{Me}}^+} \log p_i^{\text{Me}} \quad (6)$$

$$\log m_i^{t\text{-Bu}} = \frac{\sigma_{m-t\text{-Bu}}^+}{\sigma_{m-\text{Me}}^+} \log m_i^{\text{Me}} \quad (7)$$

These equations allow a test of the adherence of the data for substitution within a single molecule (1-3) or between the active sites in two molecules (4-7). The observations, presented in Table I, have been examined statistically by the least squares procedure for fit to each of these expressions, Table II.

TABLE II

STATISTICAL PARAMETERS FOR ADHERENCE OF THE SUBSTITUTION DATA TO CORRELATION EQUATIONS

| Equation | Dependent variable | Independent variable | b^a | r^b | s^c | n^d |
|----------|--------------------------|--|-------|-------|-------|-------|
| 1 | $\log p_i^{t\text{-Bu}}$ | $\log m_i^{t\text{-Bu}}$ | 2.867 | 0.985 | 0.197 | 11 |
| 2 | $\log p_i^{t\text{-Bu}}$ | $\log p_i^{t\text{-Bu}}/m_i^{t\text{-Bu}}$ | 1.488 | .992 | .285 | 11 |
| 3 | $\log m_i^{t\text{-Bu}}$ | $\log p_i^{t\text{-Bu}}/m_i^{t\text{-Bu}}$ | 0.496 | .962 | .216 | 11 |
| 4 | $\log p_i^{t\text{-Bu}}$ | S_i | 1.220 | .997 | .142 | 14 |
| 5 | $\log m_i^{t\text{-Bu}}$ | S_i | 0.409 | .978 | .166 | 11 |
| 6 | $\log p_i^{t\text{-Bu}}$ | $\log p_i^{\text{Me}}$ | 0.932 | .996 | .131 | 15 |
| 7 | $\log m_i^{t\text{-Bu}}$ | $\log m_i^{\text{Me}}$ | 1.365 | .984 | .139 | 11 |

^a Least squares slope. ^b Correlation coefficient. ^c Standard deviation. ^d Number of reactions examined.

Since the standard deviation depends on the magnitude of the data employed in the regression analysis,³⁰ the percentage error in ρ had been utilized in our examination of the applicability of the Selectivity Relationship to toluene.⁹ The data for *t*-butylbenzene were analyzed by a similar procedure. The reaction constants were determined from the partial rate factors and the adopted values for the substituent constants, $\sigma_{m-\text{Me}}^+ - 0.069$, $\sigma_{p-\text{Me}}^+ - 0.280$, $\sigma_{m-t\text{-Bu}}^+ - 0.090$ and $\sigma_{p-t\text{-Bu}}^+ - 0.260$ (see Discussion) by application of the Hammett equation (8).

$$\rho = \frac{\log k/k_0}{\sigma^+} \quad (8)$$

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

TABLE III

PERCENTAGE ERROR IN ρ FOR EACH REACTION^a

| Reaction | Reaction constant | | | | Error, % | | | |
|----------|-------------------|----------|-----------------|----------|----------|-------|-------|-------|
| | Methyl | | <i>t</i> -Butyl | | | | | |
| | ρ_m | ρ_p | ρ_m | ρ_p | | | | |
| 1 | 10.72 | 11.96 | 11.34 | 8.72 | 11.18 | 9.95 | 10.65 | 9.01 |
| 2 | 10.07 | 10.41 | 10.24 | 8.64 | 10.01 | 9.33 | 9.78 | 5.85 |
| 3 | | 9.95 | | | 9.92 | | 9.93 | 1.11 |
| 4 | 9.87 | 10.26 | 10.06 | 12.45 | 10.85 | 11.65 | 10.86 | 7.37 |
| 5 | 10.00 | 10.00 | 10.00 | 11.74 | 10.00 | 10.87 | 10.24 | 3.38 |
| 6 | 10.11 | 10.42 | 10.27 | | 10.73 | | 10.42 | 1.99 |
| 7 | 8.38 | 9.37 | 8.87 | 9.39 | 10.35 | 9.87 | 9.37 | 5.31 |
| 8 | 5.77 | 6.30 | 6.03 | 6.69 | 7.21 | 6.95 | 6.49 | 7.07 |
| 9 | 5.77 | 6.32 | 6.04 | 4.61 | 6.10 | 5.36 | 5.70 | 9.56 |
| 10 | 7.32 | 6.04 | 6.68 | | 5.62 | | 6.33 | 10.47 |
| 11 | 5.25 | 4.74 | 4.99 | | 4.59 | | 4.86 | 5.35 |
| 12 | 4.78 | 4.65 | 4.72 | 5.27 | 4.14 | 4.70 | 4.71 | 6.67 |
| 13 | 4.30 | 4.37 | 4.34 | 5.37 | 4.58 | 4.98 | 4.66 | 7.60 |
| 14 | 3.81 | 4.04 | 3.92 | 4.72 | 3.97 | 4.35 | 4.14 | 6.17 |
| 15 | 3.33 | 3.75 | 3.54 | 4.58 | 3.78 | 4.18 | 3.86 | 6.83 |

^a Based on the σ -constants $\sigma_{m-\text{Me}}^+ - 0.069$, $\sigma_{p-\text{Me}}^+ - 0.280$, $\sigma_{m-t\text{-Bu}}^+ - 0.090$ and $\sigma_{p-t\text{-Bu}}^+ - 0.260$ and the Hammett equation 8. ^b Mean value for *m*- and *p*-methyl. ^c Mean value for *m*- and *p*-butyl. ^d Average value for all substituents. ^e The mean deviation from the average value for all substituents, average value 6.44%.

The results of this analysis are summarized in Table III.

Discussion

Evaluation of a Linear Relationship.—The qualitative adherence of the data for electrophilic substitution reactions to a linear relationship was first tested by the evaluation of three ratios. The ratio $\log p_i/\log m_i$ for substitution in *t*-butylbenzene was found to be 2.89 ± 0.49 . This is significantly different from the value previously obtained for substitution in toluene, 4.04 ± 0.55 . For each reaction, Table I, the ratio is less than that for toluene. The constancy indicates the probable existence of a linear dependence between the reactivities of the *meta* and *para* positions in *t*-butylbenzene.

Next, the relationship between the methyl and *t*-butyl groups was examined. For this purpose, the ratio $\log p_i^{t\text{-Bu}}/\log p_i^{\text{Me}}$ was found to be 0.926 ± 0.054 for the 15 reactions available. The only major deviation from this value is for the nitration reaction.²⁴ The ratio for this reaction, 1.064, is larger than one. However, $\log p_i^{t\text{-Bu}}/\log m_i^{t\text{-Bu}}$ for nitration is 3.12, in good agreement with the value for the other substitution data. These observations suggest that the deviation does not arise from the orientation results, but is a consequence of an unusual value for the relative reactivities.

The ratio, $\log m_i^{t\text{-Bu}}/\log m_i^{\text{Me}}$, was evaluated to be 1.43 ± 0.20 . In addition to the results summarized in Table I, there are substitution data available for the iodination of *p*-alkylphenols and anilines.^{31,32} Although the partial rate factors for these reactions are unknown, it is clear that the rate of substitution *meta* to the 4-*t*-butyl substituent is more rapid than that for the 4-methyl substituent.^{31,32} The observations indicate that *m*-*t*-butyl groups activate the aromatic nucleus to a degree slightly greater than a *m*-methyl substituent. A single exception is reported by Jones. He found that the rate of chlorination of 4-methyl-

(31) E. Berliner, F. Berliner and I. Nelidow, *THIS JOURNAL*, **76**, 507 (1954).

(32) E. Berliner and F. Berliner, *ibid.*, **76**, 6179 (1954).

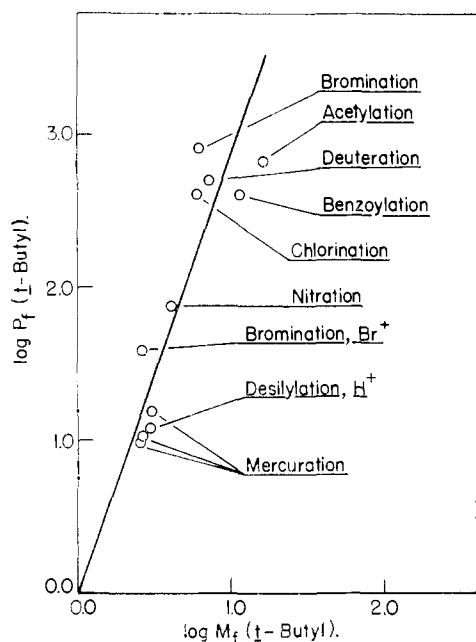


Fig. 1.—Linear relationship between $\log p_f^{t\text{-Bu}}$ and $\log m_f^{t\text{-Bu}}$ in electrophilic substitution of *t*-butylbenzene.

2-bromophenyl benzyl ethers was approximately twice that of the 4-*t*-butyl derivatives.³³ This order, however, was not observed in the mercuration³⁴ and bromination²⁰ of *p*-alkylanisoles. For these ethers, the rate of substitution has been found to be slightly greater for the *p*-*t*-butyl substituent.

The relative constancy of these ratios suggests that the *meta* and *para* reactivities in *t*-butylbenzene and between *t*-butylbenzene and toluene are governed by a common linear relationship.

The extent of this adherence to a linear function was further examined by the inspection of several graphical representations of the data. Some discussion has developed in the literature concerning the merit of the various graphical procedures for testing the linearity. The relationship was originally suggested⁶ on the basis of the adherence of experimental results to an expression of the form of equation 2. It was shown later that this expression could be derived from the Hammett equation.²⁹ The partial rate factors presented in more recent studies have been examined for their fit to the relationship by utilization of this same expression (2). In 1956, Gold and Satchell suggested that a diagram of $\log p_f$ against $\log m_f$ provided a superior method of evaluation.¹⁶

In practice, it is desirable to examine both approaches. However, there are experimental and theoretical reasons for the adoption of the $\log p_f/m_f$ treatment. Experimentally, the accurate analysis of a small quantity of the *meta* isomer in the presence of large quantities of *ortho* and *para* products provides a difficult experimental task and introduces considerable uncertainty in the analytical result. In the partial rate factor this error is compounded by the combination of this determination with two rate measurements. It is apparent that the m_f value for substitution reactions

(33) B. Jones, *J. Chem. Soc.*, 358 (1941).

(34) M. Dubeck, Ph.D. Thesis, Purdue University Library.

is not usually on a firm experimental basis. Although it is not possible to eliminate the difficulties in m_f entirely in graphical analyses of the data, it is possible to avoid the introduction of the additional inaccuracies of the kinetic measurements by the utilization of the p_f/m_f ratio. This quantity depends exclusively on the observed isomer distribution.

On a theoretical basis, the partial rate factors for *meta* and *para* substitution may be adversely influenced through the difference in stability of the π -complexes of the monosubstituted compound and benzene itself. Since the *para* partial rate factor is large, small differences in the relative stabilities of the π -complexes will have only a minor influence on $\log p_f$. For the smaller m_f , however, the influence of the π -complex in the determination of relative rate may have considerable importance. Again the utilization of p_f/m_f eliminates the error. This is true for experimental results for substitution reactions and for kinetic partial rate factors.

On the basis of these inherent difficulties, it is not surprising that a plot of $\log p_f$ against $\log p_f/m_f$ provides a more precise fit of the data to a linear relationship. For a limited amount of data, analysis on this basis is much more indicative of the potential application of a linear free energy relationship.

To illustrate this problem, diagrams have been prepared which examine the data by each method, Figs. 1–3. Figure 1 demonstrates the adherence of

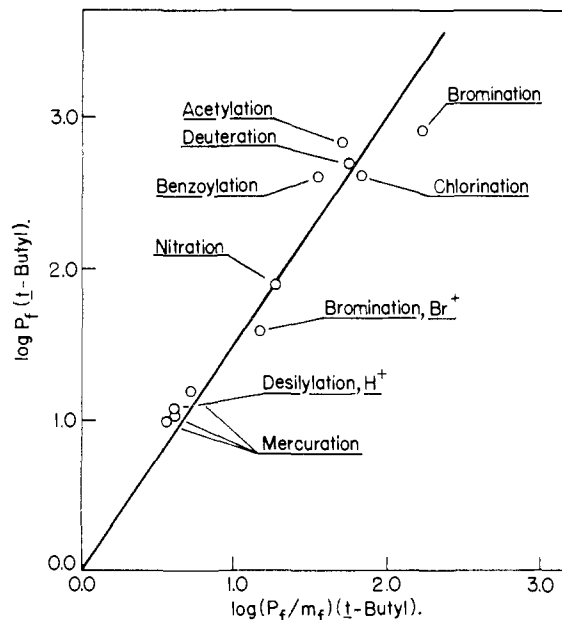


Fig. 2.—Linear relationship between $\log p_f^{t\text{-Bu}}$ and $\log (p_f^{t\text{-Bu}}/m_f^{t\text{-Bu}})$ in electrophilic substitution of *t*-butylbenzene.

the available results to an equation of the type suggested by Gold and Satchell.¹⁵ Figure 2, where $\log p_f/m_f$ for *t*-butyl is employed as the abscissa, reveals some improvement in the adherence to a linear plot. Fortunately, there is now available a third method for the evaluation of linearity. The application of S_f , $\log p_f/m_f$ for methyl, as the abscissa allows the data to be re-

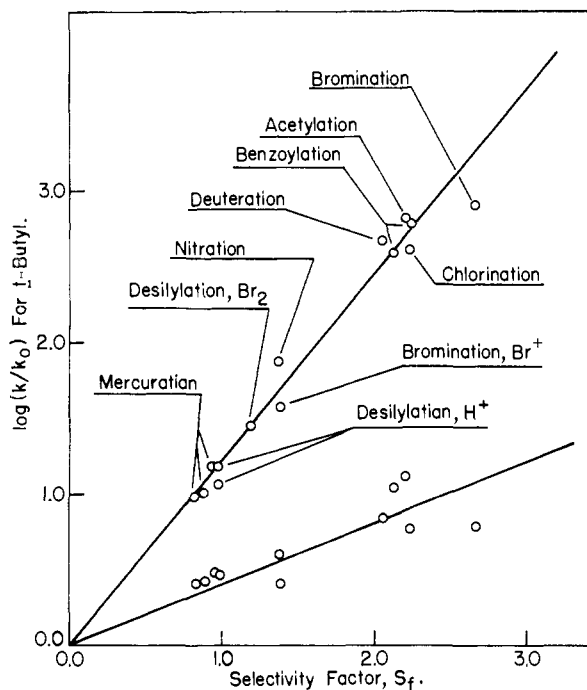


Fig. 3.—Linear relationship between $\log p_i^{t\text{-Bu}}$ and $\log m_i^{t\text{-Bu}}$ and the Selectivity Factor ($\log p_i^{\text{Me}}/\log m_i^{\text{Me}}$).

solved into two lines, Fig. 3. The *para* partial rate factors provide an excellent fit, while certain data for the *m-t*-butyl group still deviate from the correlation line. This diagram clearly indicates that the source of deviations in the first two figures was a consequence of m_t . The graphical analyses for *t*-butylbenzene indicate a linear relationship, but the agreement is not as satisfactory as had been found for toluene.³⁵

To more fully ascertain the value of this correlation, the data were examined by conventional statistical procedures. The results of this analysis are presented in Table II. In accord with the interpretation of the correlation coefficient, r , as suggested by Jaffé,³⁰ all the equations reveal a more than satisfactory relationship, $r > 0.95$. Indeed, three expressions (2, 4, 6) yield an excellent correlation, $r > 0.99$.

The observations indicate the general merit of a linear relation. To assess the quantitative value of the correlation, the percentage error in ρ was computed, Table III. The reaction constants determined from the partial rate factors for substitution in toluene reveal only minor variations. The average percentage error in ρ for the series of reaction presented in Table I is merely 3.64%. The variation in the reaction constant based on substitution data for *t*-butylbenzene is somewhat larger, 8.64%. This value is not significantly greater than that observed for 47 substitution reactions of toluene,⁹ 7.25%. When the data are examined as a consistent series of four partial rate factors the percentage error in ρ decreases to 6.44%.

The latter evaluation is particularly informative. An inspection of the reaction constants

presented in Table III reveals that those derived from *m*- and *p*-methyl and *p-t*-butyl are reasonably constant. For this sequence of reactions, the average percentage error in ρ is decreased to 4.30%. Thus, the principal source of the larger deviations observed for *t*-butylbenzene is a consequence of the variable nature of the *meta* partial rate factors for *t*-butylbenzene. The *meta* ρ -values for the mercuration (entries 13–15) and acylation (entries 4 and 5) reactions are significantly larger than the reaction constants for the other groups. On the other hand, the ρ -values for non-catalytic halogenation (entries 1 and 2) are smaller.

This analysis reveals the source of the greater deviation is a consequence of random variations in the *meta* reactivity. It is apparent that the *p-t*-butyl group adheres to a linear relationship to the same degree as the *m*- and *p*-reactivities of toluene. In particular, the excellent correlation between $\log p_i^{t\text{-Bu}}$ and $\log p_i^{\text{Me}}$ (Fig. 4) reveals that these

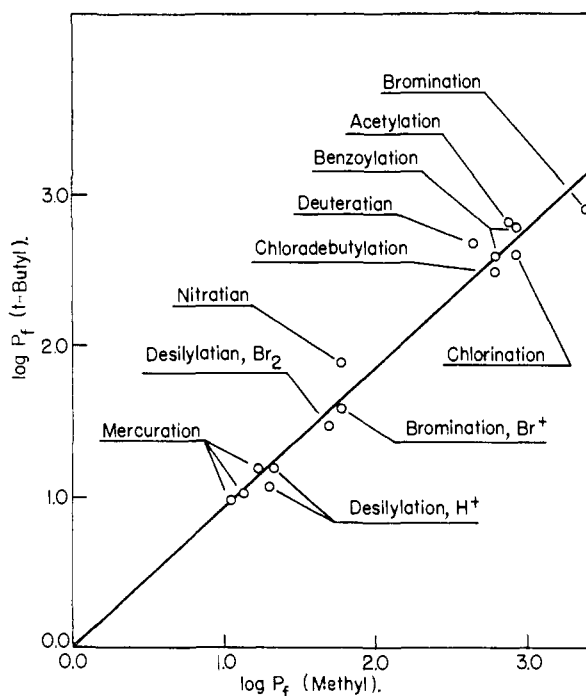


Fig. 4.—Linear relationship between $\log p_i^{t\text{-Bu}}$ and $\log p_i^{\text{Me}}$ in electrophilic substitution.

substituents respond in similar manner to the electronic demands made by the attacking reagent. These observations are quite encouraging for the extension of the Selectivity Treatment to the alkyl substituted benzenes and, possibly, to other benzene derivatives.

The deviations observed with the *m-t*-butyl results do not appear to be resolved easily. The experimental methods employed in the studies of *t*-butylbenzene and toluene were the same. Thus, the assignment of the entire deviation of the m_t values to experimental uncertainty does not appear justified. However, because of the experimental uncertainties, the evaluation of explicit

(35) Compare Fig. 2 with Fig. 1, ref. 9.

causes for the deviations is rendered difficult.³⁶ Whereas the results for mercuration appear greater than anticipated, they are not greater than the experimental uncertainty in the observed m_f value itself (10%). The observations for acylation and halogenation do, however, appear to be beyond the limit of experimental error.³⁷

Evaluation of the Sigma Constants.—In our earlier analysis of the application of the Selectivity Relationship to the substitution reactions of toluene,⁹ σ^+_{m-Me} was assigned as -0.069 . The adoption of this value allowed the calculation of $\sigma^+_{p-Me} = -0.280$. These constants and the slopes of the regression lines (4-7) provide the necessary information for the calculation of σ -constants for the *t*-butyl group.

As discussed, the *p*-*t*-butyl group obeys a linear relationship to a higher degree than does the *meta* substituent. The assignment of a σ -constant for the *p*-*t*-butyl group will be made first in order to provide additional methods for the estimation of a constant for *m*-*t*-butyl. Values of the substituent constant for *p*-*t*-butyl, based on the σ -values for *m*- and *p*-methyl and the slopes of the regression lines, are summarized in Table IV. Another estimate of this quality is possible from the $\log p_f^{t-Bu}/\log p_f^{Me}$ ratio. This approach yields the σ -constant -0.259 ± 0.015 . On the basis of this value and those derived from the statistical slopes, the σ^+_{p-t-Bu} constant is assigned the value -0.260 ± 0.15 . This constant is well within experimental error of the result based upon the *t*-cumyl chloride solvolysis data,¹⁰⁻¹² -0.256 .

The σ^+_{m-t-Bu} constants provided by the regression equations are summarized in Table IV. In addition to these values another estimate of the constant is possible on the basis of the ratio $\log m_f^{t-Bu}/\log m_f^{Me}$. This provides the σ^+_{m-t-Bu} constant -0.099 ± 0.014 . The utilization of

(36) Calculation of m_f from the mean ρ -values, Table III, $\sigma_{m-t-Bu} = -0.090$ yields an average percentage error in the calculated m_f of 19.1%. Five reactions reveal deviations which probably are beyond the experimental error; bromination (49.4%), chlorination (26.5%), acetylation (27.6%), benzoylation (26.7%) and acid-catalyzed bromination (25.4%).

(37) There is evidence that these variations in m_f^{t-Bu} arise from changes in the nature of the transition states in different substitution reactions. The question is currently under investigation with Dr. G. Marino and we hope to communicate the results shortly.

TABLE IV

σ -CONSTANTS FOR *m*- AND *p*-*t*-BUTYL SUBSTITUENTS IN ELECTROPHILIC REACTIONS^a

| Equation | Slope | σ^+_{p-t-Bu} | σ^+_{m-t-Bu} |
|----------|---|---------------------|---------------------|
| 1 | $\sigma^+_{p-t-Bu}/\sigma^+_{m-t-Bu}$ | | -0.091 |
| 2 | $\sigma^+_{p-t-Bu}/(\sigma^+_{p-t-Bu} - \sigma^+_{m-t-Bu})$ | | -0.086 |
| 3 | $\sigma^+_{m-t-Bu}/(\sigma^+_{p-t-Bu} - \sigma^+_{m-t-Bu})$ | | -0.086 |
| 4 | $\sigma^+_{p-t-Bu}/(\sigma^+_{p-Me} - \sigma^+_{m-Me})$ | -0.257 | |
| 5 | $\sigma^+_{m-t-Bu}/(\sigma^+_{p-Me} - \sigma^+_{m-Me})$ | | -0.086 |
| 6 | $\sigma^+_{p-t-Bu}/\sigma^+_{p-Me}$ | -0.261 | |
| 7 | $\sigma^+_{m-t-Bu}/\sigma^+_{m-Me}$ | | -0.099 |

^a Based on the values $\sigma^+_{p-Me} = -0.280$, $\sigma^+_{m-Me} = -0.069$, and, where necessary, $\sigma^+_{p-t-Bu} = -0.260$.

$\log p_f^{t-Bu}/\log m_f^{t-Bu}$ indicates the value to be -0.090 ± 0.013 . On the basis of these different approaches, the σ^+_{m-t-Bu} constant is estimated as -0.090 ± 0.020 . This result is not in close agreement with the constant determined from the *t*-cumyl chloride studies,¹⁰⁻¹² -0.058 .³⁸ The value determined for the electrophilic reactions is within experimental error of the Hammett parameter, $\sigma_{m-t-Bu} = 0.10 \pm 0.03$.

Summary.—The electrophilic substitution reactions of *t*-butylbenzene appear to obey the Selectivity Relationship with satisfactory over-all precision. On the basis of the methods for the evaluation of the relationship, the *para* reactivities adhere to the relationship to the same degree as found for the corresponding reactions of toluene. Although the important nitration reaction reveals a deviation, the result is not sufficiently different from anticipated behavior to introduce a serious error. The *meta* partial rate factors reveal deviations which possibly are beyond experimental uncertainty. However, in this instance the importance of the stability of π -complexes and solution effects remains to be established.

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(38) Whereas *m*-*t*-butylcumyl chloride undergoes solvolysis in 90% acetone at a rate slightly slower than that of the *m*-methyl derivative, in alcohol solvents the reverse is true. See Y. Okamoto, T. Inukai and H. C. Brown, THIS JOURNAL, **80**, 4972 (1958). Consequently, the solvolyses in the alcoholic solvents are in closer agreement with the value for σ^+_{m-t-Bu} derived from the substitution data.