mated from the absorption at 9.61 $\mu$ (trans isomer) and 9.85 $\mu$[15] (cis isomer) by the method described for analyzing mixtures of 1- and 3-$t$-butylcyclohexene. The acetate isolated from the acetolysis of the trans-toluenesulfonate II was found to be 53% cis-acetate and that obtained from the cis-toluenesulfonate I was found to be 92% cis-acetate. Because of the impurity in the acetate fraction the accuracy of these determinations is uncertain. Moreover it is possible that some of the acetate results from esterification of small amounts of 2-$t$-butylcyclohexanol which may have been present in some of the samples of $p$-toluenesulfonate that were solvolyzed.

(15) The spectrum of cis-2-butylcyclohexyl acetate has a strong band at 10.4 $\mu$ (not present in the spectrum of the trans isomer); however, the impurity interfered with the absorption at this wave length.

The reaction products were carefully examined with provisions for trapping gaseous products; however, cleavage products, e.g., cyclohexene and isobutene, or rearranged products were not present in detectable quantities.

**B. Ethanolysis.**—A solution of 7.34 g. (0.024 mole) of trans-$p$-toluenesulfonate II in 190 ml. of 0.13 $N$ sodium ethoxide in absolute ethanol was heated to 50° for 18 hours (about 10 half-lives). The products were extracted and isolated by the same procedure used for the acetolyses. The 3.1 g. (95%) of olefin was found to be an apparently pure binary mixture of 1- and 3-$t$-butylcyclohexene consisting of 53% of the 1-isomer. The products resulting from the solvolysis of the cis-$p$-toluenesulfonate II were examined in the same way. There was no evidence for the formation of rearrangement or cleavage products.

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# The Application of Taft's Equation to Polar Effects in Solvolyses

BY ANDREW STREITWIESER, JR.

The Taft equation, $\log (k/k_0) = \sigma^*\rho^*$, is applied to several solvolytic systems with satisfactory results. Driving forces for anchimeric assistance are derived from the correlations.

One criterion for neighboring group participation in solvolytic reactions is an enhancement of rate over that expected in the absence of participation.[1]

The application of this criterion requires a good estimate of the unassisted solvolysis rate. One elegant approach is that of Winstein, Grunwald and Ingraham,[2,3] who compared the acetolysis rates of cis- and trans-2-substituted cyclohexyl brosylates. Participation is geometrically impossible for the cis cases; hence, the solvolysis rates of the cis compounds may be taken as approximations to the unassisted rates of the trans isomers. Excesses of rates over these estimates are then attributable to anchimeric[1] assistance. Conformation effects are known to be significant in alkyl cyclohexyl systems[4]; however, the fact that the acetolysis rates of cis- and trans-1,2-di-$p$-bromobenzenesulfonoxycyclohexane, in which participation does not occur, differ by a factor of only 1.12,[2] suggests that dipole interactions tend to cancel the differences due to axial and equatorial configurations in those cases in which the 2-substituent is highly polar. In other systems, Winstein and Grunwald[5] have used calculations based on simple electrostatic principles to estimate polar effects on solvolysis rates. The method requires a number of approximations and cannot be applied to alkyl or aryl substituents. The wide utility of Taft's polar substituent constants, $\sigma^*$,[6] (which are an extension of Branch and Calvin's[7] earlier concept of inductive parameters) suggests an application to solvolytic systems. Sufficient data are available for a test

(1) S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).

(2) S. Winstein, E. Grunwald and L. L. Ingraham, ibid., **70**, 821 (1948).

(3) E. Grunwald, ibid., **73**, 5458 (1951).

(4) S. Winstein and N. J. Holness, ibid., **77**, 5562 (1955).

(5) S. Winstein and E. Grunwald, ibid., **70**, 828 (1948).

(6) R. W. Taft, Jr., ibid., (a) **74**, 2729 (1952); (b) **74**, 3120 (1952); (c) **75**, 4231 (1953); (d) **75**, 4534 (1953); (e) **75**, 4538 (1953).

(7) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1941, p. 201.

in several solvolytic systems of Taft's equation: $\log (k/k_0) = \sigma^*\rho^*$.

The literature contains much rate data on the solvolyses of secondary carbinyl sulfonic esters in acetic acid. Using the data in Table I, the reactivities of the secondary alkyl and cis-2-substituted
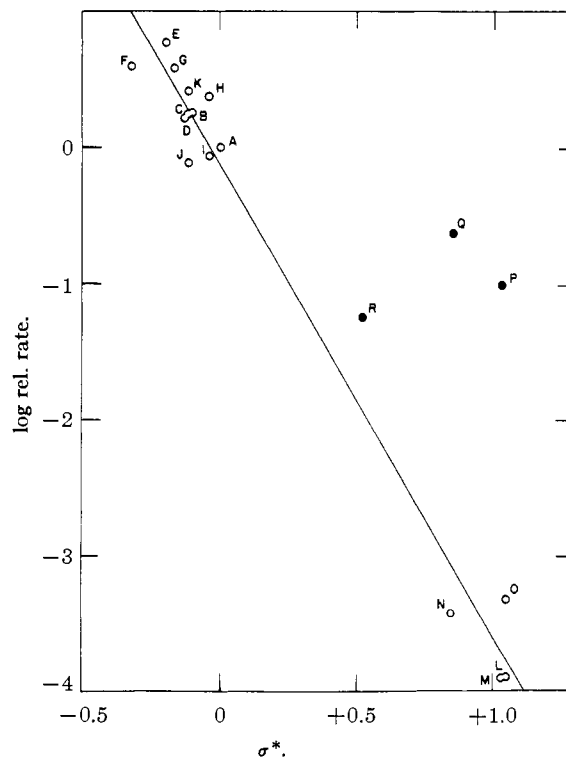


Fig. 1.—Correlation of secondary carbinyl sulfonate acetolysis rates with polar substituent constants, $\sigma^*$. The least squares line is based on the open circles. Closed circles refer to compounds which involve anchimeric assistance. Letters refer to compounds in Table I.

### TABLE I
### RELATIVE ACETOLYSIS RATES OF SECONDARY CARBINYL SULFONATES

| Letter in Fig. 1 | Compound alkyl brosylate | Rate relative to—— | | $\sigma^{*a}$ | Rate enhancement[b] | Refs. |
| | | $i$-Propyl brosylate 70° | Cyclohexyl brosylate 75° | | | |
|---|---|---|---|---|---|---|
| A | Isopropyl | 1.00 | | 0.00 | .. | 8 |
| A | Cyclohexyl | | 1.00 | .00 | .. | 2 |
| B | 2-Butyl | 1.8 | | − .100 | .. | 9, 10 |
| C | 2-Pentyl | 1.8 | | − .115 | .. | 9 |
| D | 4-Methyl-2-pentyl | 1.6 | | − .125 | .. | 9 |
| E | 3-Methyl-2-butyl | 5.9 | | − .200 | .. | 10 |
| F | 3,3-Dimethyl-2-butyl | 3.9 | | − .320 | .. | 10 |
| G | 4,4-Dimethyl-2-pentyl | 3.8 | | − .165 | .. | 9 |
| H | $cis$-4-$t$-Butylcyclohexyl | | 2.39[c] | − .01[d] | .. | 7 |
| I | $trans$-4-$t$-Butylcyclohexyl | | .88[c] | − .01[d] | .. | 7 |
| J | $cis$-3-$t$-Butylcyclohexyl | | .78[c] | − .04[d,j] | .. | 7 |
| K | $trans$-3-$t$-Butylcyclohexyl | | 2.56[c] | − .04[d,j] | .. | 7 |
| L | $cis$-2-Chlorocyclohexyl | | $1.27 \times 10^{-4}$ | +1.050 | .. | 3 |
| M | $cis$-2-Bromocyclohexyl | | $1.24 \times 10^{-4}$ | +1.030 | .. | 3 |
| N | $cis$-2-Acetoxycyclohexyl | | $3.79 \times 10^{-4}$ | + .85 | .. | 2 |
| O | $trans$-2-Chlorocyclohexyl | | $4.80 \times 10^{-4}$ | +1.050 | .. | 3 |
| P | $trans$-2-Bromocyclohexyl | | 0.101 | +1.030 | 450 | 2 |
| Q | $trans$-2-Acetoxycyclohexyl | | .240 | +0.85 | 320 | 2 |
| R | $trans$-2-Methoxycyclohexyl | | .057 | + .52 | 4.5 | 2 |
| | $trans$-2-Iodocyclohexyl | | 1170[c,e] | + .85 | 1,500,000 | 2 |
| | $erythro$-3-Phenyl-2-butyl | 1.04[f,g] | | + .11 | 3.5 | 11 |
| | $threo$-3-Phenyl-2-butyl | 1.19[f,g] | | + .11 | 4.0 | 11 |
| | 3-Methyl-3-phenyl-2-butyl | 65[f] | | + .01 | 94 | 11 |
| | 1,1-Diphenyl-2-propyl | 1.64[f] | | + .405 | 57 | 11 |
| | 1-Phenyl-2-propyl | 0.29[f] | | + .215 | 2.2 | 11 |
| | 1-$p$-Anisyl-2-propyl | 6.5[f,h] | | + .12[i] | 23 | 12 |
| | 4-Phenyl-3-hexyl | 4.14[f] | | + .015 | 6.3 | 13 |
| | 3-$p$-Anisyl-2-butyl | 81[f,g] | | + .02[i] | 130 | 12 |

[a] Reference 5c. [b] $k_{observed}/k_{calculated}$. [c] Rates of the tosylates relative to cyclohexyl tosylate. [d] Calculated using the inductive parameter, 2.8.[5c] [e] At 23.6°. [f] At 50°. [g] $k_{ROTs}/k_{ROBs}$ was taken as 0.32. [h] $k_{ROTs}/k_{ROBs}$ was taken as 0.28. [i] $\sigma^*$ for $p$-anisylCH$_2$– was taken as +0.12. [j] These points are slightly displaced in Fig. 2.

cyclohexyl systems define a straight line when plotted against the appropriate $\sigma^*$-values (Fig. 1). The procedure involved in handling the many simple alkyl systems requires comment. In such systems, the inductive effect is rather small (low

(8) E. Grunwald and S. Winstein, THIS JOURNAL, 70, 846 (1948).

(9) H. C. Brown and M. Nakagawa, ibid., 77, 3614 (1955).

(10) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, ibid., 74, 1127 (1952).

(11) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, ibid., 74, 1113 (1952).

(12) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, ibid., 74, 1140 (1952).

(13) D. J. Cram and F. A. Abd Elhafez, ibid., 75, 3189 (1953).

(14) E. D. Hughes, J. Chem. Soc., 255 (1935).

(15) H. C. Brown and R. S. Fletcher, THIS JOURNAL, 71, 1845 (1949).

(16) H. C. Brown, R. S. Fletcher and R. B. Johannesen, ibid., 73, 212 (1951).

(17) E. D. Hughes, C. K. Ingold and V. J. Shiner, Jr., J. Chem. Soc., 382 (1953).

(18) V. J. Shiner, Jr., THIS JOURNAL: (a) 75, 2925 (1953); (b) 76, 1603 (1954).

(19) H. C. Brown and R. S. Fletcher, ibid., 73, 1317 (1951).

(20) H. Kwart and W. C. Wilson, ibid., 75, 6147 (1953).

(21) H. Nilsson and L. Smith, Z. physik. Chem., 166A, 136 (1933).

(22) C. G. Swain and S. D. Ross, THIS JOURNAL, 68, 658 (1946).

(23) H. C. Brown, M. S. Kharasch and T. H. Chao, ibid., 62, 3435 (1940).

(24) D. V. Tishchenko, J. Gen. Chem. (U.S.S.R.), 9, 1380 (1939).

(25) C. M. Suter and H. D. Zook, THIS JOURNAL, 66, 738 (1944).

(26) P. Petrenko-Kritschenko, Ber., 61, 845 (1928).

(27) H. C. Brown and H. L. Berneis, THIS JOURNAL, 75, 10 (1953).

(28) S. Winstein and B. K. Morse, ibid., 74, 1133 (1952).

(29) K. A. Cooper, E. D. Hughes, C. K. Ingold, G. A. Maw and B. J. MacNulty, J. Chem. Soc., 2049 (1948).

$\sigma^*$) and such other effects as steric hindrance to solvation, steric strains and hyperconjugation probably play a significant role. Consequently, one could say that the parent compounds must fit on the correlation line, draw the line accordingly and see how well the other alkyl compounds fit; or, one could include all of the available alkyl compounds in a least squares fitting process with the hope that the use of a large number of compounds would tend to cancel effects other than inductive. The latter procedure was arbitrarily adopted in this paper. In this particular case, either procedure would have given essentially the same results for the parent compounds (A in Fig. 1) lie very close to the correlation line. Taken as a whole, the simple alkyl groups appear to fit rather well. The exceptional cases (F, H and J) are ones for which conformational effects or steric hindrances to solvation are probably significant.

The distances of points above the line are measures of anchimeric assistance. Such measures can now be obtained for groups which have not been scrutinized by the cyclohexane method, although, clearly, small deviations from the line should not be regarded as significant. A number of derived driving forces for participation are included in Table I. The numbers differ quantitatively from those estimated by Winstein[5]; however, the differences are not important enough to affect his derived arguments.

<div align="center">

Table II

Relative Solvolysis Rates of Tertiary Halides in Aqueous Ethanol

</div>

| Letter in Fig. 2 | Compound | Rel. rate 80% ethanol 25° | $\sigma^{*a}$ | Rate enhance- ment[b] | References |
|---|---|---|---|---|---|
| A | $(CH_3)_3CCl$ | 1.00 | 0.000 | | 14, 15, 16, 17 |
| B | $(CH_3)_2CClC_2H_5$ | 1.65 | $-$ .100 | | 14, 15, 18a |
| C | $(CH_3)_2CClCH_2CH_2CH_3$ | 1.58 | $-$ .115 | | 15 |
| D | $(CH_3)_2CCl(CH_2)_3CH_3$ | 1.43 | $-$ .130 | | 15 |
| E | $CH_3CCl(C_2H_5)_2$ | 2.58 | $-$ .200 | | 14, 15 |
| F | $(CH_3)_2CClCH(CH_3)_2$ | 0.95 | $-$ .190 | | 18b |
| G | $(CH_3)_2CClC(CH_3)_3$ | 1.21 | $-$ .300 | | 15 |
| H | $(C_2H_5)_3CCl$ | 3.02 | $-$ .300 | | 14, 15 |
| I | $CH_3CCl(CH(CH_3)_2)_2$ | 14.2 | $-$ .38 | | 19 |
| J | $(C_2H_5)_2CClCH_2OH$ | $14.045^c$ | $+$ .365 | | 20, 21, 22 |
| K | $(CH_3)_2CClCH_2OH$ | $6.6 \times 10^{-3c}$ | $+$ .555 | | 20, 21, 22 |
| L | $(CH_3)_2CClCOH(CH_3)_2$ | $6.0 \times 10^{-3c}$ | $+$ .365 | | 20, 21, 22 |
| M | $(CH_3)_2CClCHOHCH_3$ | $3.4 \times 10^{-3c}$ | $+$ .455 | | 20, 21, 22 |
| N | $C_2H_5(CH_3)CClCH_2Cl$ | $4.7 \times 10^{-4d}$ | $+$ .950 | | 23 |
| O | $(CH_3)_2CClCH_2Cl$ | $2.53 \times 10^{-4d}$ | $+1.050$ | | 23 |
| P | $(CH_3)_2CClCCl(CH_3)_2$ | $5.8 \times 10^{-4e,f}$ | $+0.860$ | | 5, 24 |
| Q | $(CH_3)_2CBrCH_2Br$ | $1.6 \times 10^{-4g}$ | $+1.030$ | | 5 |
| R | $(CH_3)_2CBrCHBrCH_3$ | $2.1 \times 10^{-3g}$ | $+0.930$ | 6 | 25 |
| S | $(CH_3)_2CBrCBr(CH_3)_2$ | $0.0325^{e,h}$ | $+$ .840 | 46 | 26 |
| T | $(CH_3)_2CClCH_2I$ | .486 | $+$ .85 | 740 | 5 |
| | $(CH_3)_2CClCH(CH_3)C_6H_5$ | $.17^i$ | $+$ .11 | 1.0 | 28, 29 |
| | $(CH_3)_2CClCH_2C(CH_3)_3$ | 21.6 | $-$ .165 | 15 | 14, 15 |
| | $CH_3CCl(CH_2C(CH_3)_3)_2$ | 574 | $-$ .330 | 120 | 27 |

[a] Reference 5c. [b] $k_{observed}/k_{calculated}$. [c] In water at 18°. The rate of $t$-butyl chloride was extrapolated from 25°, using $E^{\neq} = 22.5$ kcal./mole. [d] At 79°. [e] Rates were divided by the statistical factor of two. [f] At 100°. [g] Rate relative to $t$-butyl bromide. [h] Rate relative to $t$-butyl bromide in 76% aq. ethanol at 18.5°. [i] At 50°.

The data for a number of tertiary carbinyl chlorides in Table II have been plotted in Fig. 2. Because neighboring chlorine does not manifest significant anchimeric assistance in secondary cases (Table I and Fig. 1), none is expected in tertiary cases.[5] The solvolysis rates of the tertiary dichlorides are, consequently, rates of normal solvolyses and may be used to define a polar effect correlation line. In this system it is apparent from Fig. 2 that neighboring hydroxyl group also does not participate and compounds which contain this group were used to further define the correlation line. The alkyl groups were averaged as above. The deviations are more serious with the tertiary compounds and the parent compound, $t$-butyl chloride (A in Fig. 2) deviates from the correlation line by an amount which corresponds to a rate factor of about 2.4. Deviations from the correlation line by rate factors of less than about three should not be regarded, therefore, as usefully significant. The rate enhancements in the cases of dimethylneopentylcarbinyl chloride and methyl-dineopentylcarbinyl chloride, 15 and 120-fold, respectively, are far larger than this estimated uncertainty, and are in agreement with Brown's view that steric acceleration of rate is important in these cases.[15,27] The poor fit of the chlorohydrin compounds (J, K, L and M in Table II) may either result from limitations of the method or may be due to errors involved in extrapolating from a different solvent and a different temperature. The rate enhancements calculated by this method (Table II) differ in an unimportant manner from those computed by Winstein and Grunwald.[5]

The recent data of Laughton and Robertson[30]

(30) P. M. Laughton and R. E. Robertson, Can. J. Chem., 33, 1207 (1955).

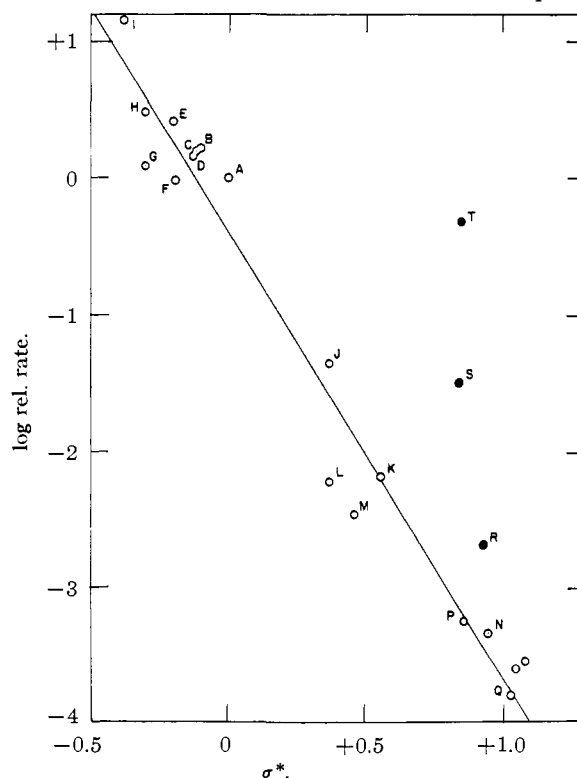on the alcoholyses of primary carbinyl sulfonate esters in Table III have been used to obtain a polar



Fig. 2.—Correlation of solvolysis rates of tertiary halides in 80% ethanol with polar substituent constants, $\sigma^*$. The least squares line is based on the open circles. Closed circles refer to compounds which involve anchimeric assistance. Letters refer to compounds in Table II.

effect correlation line in this system (Fig. 3). The fit is excellent (Table IV). Two significant features of this correlation which deserve comment are the slope of the line (value of $\rho^*$) and the marked deviation of the ethyl compound from the line. The alcoholyses of primary alkyl sulfonates undoubtedly require a significant nucleophilic contribution by solvent at the transition state—in the language of Winstein, Grunwald and Jones,[31] the solvolysis has considerable N character; consequently, it is important that the steric requirements at the reacting center be the same for the compounds compared. The faster rate for the ethyl compound, like the relative rates of direct displacement reactions, is undoubtedly due to lesser steric hindrance to nucleophilic attack. The amount of positive charge developed at the primary carbon in these solvolyses is much less than in more limiting[31] solvolyses; hence, the slope of the correlation line is much less (Table IV). The close similarity of the slopes in the acetolyses of secondary carbinyl brosylates and the hydrolyses of tertiary halides is consistent with both of these reaction systems being limiting.[31]
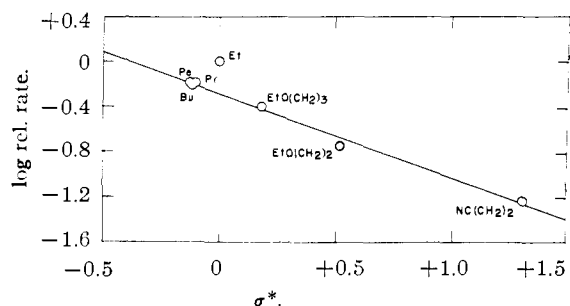


Fig. 3.—Correlation of alcoholysis rates of primary sulfonates with polar substituent constants, $\sigma^*$. The ethyl point was not used to define the least squares line.

The correlations obtained have been used to calculate rate enhancements in systems which involve a neighboring aryl group. Winstein[11] has assigned a rate-retarding inductive effect of 10-fold for each neighboring phenyl group. This value is rather close to that which is obtained by use of the $\sigma^*$-value for a neighboring phenyl substituent when $\rho^*$ has a value of about $-3$ to $-3.5$. In solvolysis systems which are not limiting, a factor of 10 is too large. In the present treatment, no important anchimeric effects are found for the ethanolyses of $\beta$-phenyl- and $\beta$-anisylethyl tosylates (Table III).

Application of the Taft equation to direct displacement reactions is limited by the scarcity of good data. Apparently, the only data free from objection of one sort or another are the recent results of Hine and Brader[32] on the reaction of $n$-propyl, $n$-butyl and ethylene halides with sodium

(31) S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

(32) J. Hine and W. H. Brader, Jr., *ibid.*, **75**, 3964 (1953).

TABLE III

RELATIVE ALCOHOLYSIS RATES OF PRIMARY TOSYLATES

| Alkyl tosylate | Rel. rate $100^{\circ}_{30}$ | $\sigma^{*a}$ | $k_{obsd.}/k_{calcd.}$ |
|---|---|---|---|
| $C_2H_5-$ | 1.00 | 0.000 | |
| $CH_3CH_2CH_2-$ | $.64^b$ | $-.100$ | |
| $CH_3(CH_2)_3-$ | $.61^b$ | $-.115$ | |
| $CH_3(CH_2)_4-$ | $.65^b$ | $-.130$ | |
| $C_2H_5OCH_2CH_2-$ | .18 | $+.52^c$ | |
| $C_2H_5OCH_2CH_2CH_2-$ | .40 | $+.185^d$ | |
| $NCCH_2CH_2-$ | .059 | $+1.30$ | |
| $C_6H_5CH_2CH_2-$ | $.26^e$ | $+0.215$ | 0.72 |
| $p-CH_3OC_6H_4CH_2CH_2-$ | $.30^e$ | $+.12$ | 0.71 |
| $o-CH_3OC_6H_4CH_2CH_2-$ | $.49^e$ | $+.075$ | 1.1 |

$^a$ Reference 6c. $^b$ Rate of the benzenesulfonate relative to ethyl benzenesulfonate. $^c$ $\sigma^*$ for $CH_3OCH_2-$ substituent was used. $^d$ Calculated from the value for $CH_3OCH_2-$ substituent using the inductive parameter, 2.8.[6c] $^e$ At 75°; ref. 1.

thiophenolate in methanol. The steric requirements at the reacting center are probably closely the same for all of these halides and the rate differences may be taken as measures of the effect of inductive forces alone. The $\rho^*$ for this reaction, $-0.606$ (Table IV), corresponds to the production of only a small amount of positive charge at the

TABLE IV

CORRELATIONS OF RATES OF DISPLACEMENT REACTIONS WITH POLAR SUBSTITUENT CONSTANTS

| System | $\rho^*$ | $r^a$ | $n$ |
|---|---|---|---|
| $R_2CHOBs$, AcOH, 70–75° | $-3.49$ | 0.17 | 15 |
| $R_3CCl$, 80% EtOH, 25° | $-3.29$ | .22 | 17 |
| $RCH_2OTs$, EtOH, 100° | $-0.742$ | .027 | 6 |
| $XCH_2CH_2Br$, $C_6H_5S^-$, MeOH, 20° | $-0.606$ | .024 | $5^b$ |

$^a$ Probable error. $^b$ X = Me, Et, F, Br and Cl.

transition state. The magnitude of the slope is rather close to that for the alcoholyses of primary sulfonates. It is important to note that the effect of polarity on displacement rate is in the same direction as in the solvolyses and is opposite to the direction assumed by Hughes and Ingold.[33] However, the correlation line is determined by two separated groups of points and cannot be used as evidence that the present treatment is valid. Further rate data for this reaction would be desirable.

NOTE ADDED IN PROOF: This SN2 series has been extended to the system $X(CH_2)_3Br$ [J. Hine, S. J. Ehrenson and W. H. Brader, Jr., THIS JOURNAL, **78**, 2282 (1956)]. Using the value for $\rho^*$ in Table IV, the calculated and observed logarithms of the rates relative to $n$-butyl bromide at 20° for different X groups are, respectively, Br, $-0.22$, $+0.05$; Cl, $-0.23$, $-0.02$; F, 0.24, $-0.15$. As the differences due to inductive effects become smaller, other effects become of overriding importance.

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(33) P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold and J. D. H. MacKie, *J. Chem. Soc.*, 3200 (1955).