dried ($MgSO_4$), and concentrated under reduced pressure. The residue was flash chromatographed (SiO_2, 32 × 8.5 cm, 10% ether/hexane → 20% ether/hexane) to afford the brominated diol **20** as a white foam after drying under vacuum: 21.08 g (93%); ^{1}H NMR δ 2.30 (s, 3 H, $ArCH_3$), 2.36 (s, 6 H, $ArCH_3$), 5.06 (s, 2 H, -OC*H*$_2$Ph), 6.20 (s, 1 H, OH), 6.73 (s, 1 H, OH), 6.96–7.33 (m, 12 H, ArH); MS, *m/e*, M^+ (^{79}Br) 488. Anal. Calcd for $C_{28}H_{25}BrO_3$: C, H, and Br.

3-Bromo-2,2′-dimethoxy-5,5′,5″-trimethyl-2″-(phentylmethoxy)-1,1′:3′,1″-terphenyl (21). To 13.31 g (27.20 mmol) of diol **20** in 400 mL of THF was added 50 mL of water and 7.0 g (175 mmol) of NaOH. This mixture was stirred for 15 min, and then 10.3 mL (109 mmol) of $(CH_3)_2SO_4$ was added. The reaction mixture was refluxed for 1.5 h, cooled, quenched with concentrated NH_4OH, and partitioned between 200 mL of ether and 100 mL of water. The organic phase was washed with 100 mL of water and 100 mL of brine. The combined aqueous phases were extracted with 50 mL of ether, and the combined organic phases were dried ($MgSO_4$). The solvent was removed in vacuo, and the residue was dried at 100 °C under vacuum to give the ether **21** as a slightly yellow viscous oil, pure enough for use in subsequent reactions (14.09 g, >99%). An analytical sample prepared via preparatory TLC (SiO_2, 10% ether/hexane) gave **21** as a viscous oil: ^{1}H NMR δ 2.29 (s, 3 H, $ArCH_3$), 2.32 (s, 3 H, $ArCH_3$), 2.34 (s, 3 H, $ArCH_3$), 3.19 (s, 3 H, OCH_3), 3.48 (s, 3 H, OCH_3), 5.03 (s, 2 H, -OC*H*$_2$Ph), 6.90–7.35 (m, 12 H, ArH); MS, *m/e*, M^+ (^{79}Br) 516. Anal. Calcd for $C_{30}H_{29}BrO_3$: C, H, and Br.

2,2′′′′′-Bis(phenylmethoxy)-2′,2″,2‴,2′′′′-tetramethoxy-5,5′,5″,5‴,5′′′′,5′′′′′-hexamethyl-1,1′:3′,1″:3″,1‴:3‴,1′′′′:3′′′′,1′′′′′-sexiphenyl (22). To a solution of 2.88 g (5.57 mmol) of triphenyl **21** in 75 mL of dry THF at −78 °C was added 5.88 mmol of butyllithium in hexane. The light yellow solution was stirred 10 min at −78 °C and then transferred via cannula into a refluxing solution of 3.95 g (11.18 mmol) of $Fe(acac)_3$ in 100 mL of benzene. The reaction mixture was refluxed for 2.5 h, cooled, and partitioned between 250 mL of ether and 200 mL of 1/1 concentrated hydrochloric acid/water. The organic phase was washed with 4 × 125 mL of water. The combined aqueous washings were extracted with 150 mL of ether, and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (medium pressure, SiO_2, columns A + B, 10% ether/hexane) to provide sexiphenyl **22** as a white foam after drying under vacuum: 1.25 g (51%); ^{1}H NMR δ 2.31 (s, 3 H, $ArCH_3$), 2.34 (s, 6 H, $ArCH_3$), 3.24 (s, 3 H, OCH_3), 3.28 (s, 3 H, OCH_3), 5.02 (s, 2 H, -OC*H*$_2$Ph), 6.88–7.27 (m, 12 H, ArH); MS, *m/e*, M^+ 874. Anal. Calcd for $C_{60}H_{58}O_6$: C and H.

2′,2″,2‴,2′′′′-Tetramethoxy-5,5′,5″,5‴,5′′′′,5′′′′′-hexamethyl-[1,1′:3′,1″:3″,1‴:3‴,1′′′′:3′′′′,1′′′′′-sexiphenyl]-2,2′′′′′-diol (23). A mixture of 1.25 g (1.43 mmol) of sexiphenyl **22**, 750 mg of 10% palladium/carbon, 25 mL of ethyl acetate, and 25 mL of ethanol was hydrogenated under 2.5 atm of hydrogen in a Parr apparatus for 1 h at 25 °C. The reaction mixture was filtered through Whatman No. 50 hardened filter paper and concentrated under reduced pressure to afford the diol **23** as a white foam after drying under vacuum: 0.96 g (97%); ^{1}H NMR δ 2.35 (s, 3 H, $ArCH_3$), 2.38 (s, 3 H, $ArCH_3$), 2.40 (s, 3 H, $ArCH_3$), 3.31 (s, 3 H, OCH_3), 3.35 (s, 3 H, OCH_3), 6.91–7.25 (m, 14 H, ArH); MS, *m/e*, M^+ 694. Anal. Calcd for $C_{46}H_{46}O_6$: C and H.

30,35-Dihydro-37,38,39,40-tetramethoxy-3,7,12,17,22,26-hexamethyl-5,9:10,14,15,19:20,24-tetramethenotribenzo[*c*,*g*,*c*][1,6]dioxacyclotriacontin (9). To a refluxing suspension of 351 mg (w/oil) of NaH (7.31 mmol) in 250 mL of THF was added dropwise with stirring a solution of 960 mg of diol **23** (1.382 mmol) and 188 mg (0.71 mmol) of 1,2-bis(bromomethyl)benzene in 200 mL of THF under high dilution over an 88-h period. The reaction mixture was refluxed an additional 103 h, cooled, and quenched with water. The solvent was removed in vacuo, and the residue was partitioned between 300 mL of CH_2Cl_2 and 100 mL of water. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed (medium pressure, SiO_2, column B, 15% ether/hexane) to yield the cycle as a white solid, 220 mg (20%). An analytical sample was prepared by recrystallization from CH_2Cl_2/methanol to give white crystals: mp 263–271 °C; ^{1}H NMR δ 2.33 (s, 6 H, $ArCH_3$), 2.35 (s, 3 H, $ArCH_3$), 2.78 (s, 3 H, OCH_3), 3.16 (s, 3 H, OCH_3), 4.90 (s, 2 H, J = 13.3 Hz, OCH_2), 5.15 (d, 2 H, J = 13.3 Hz, OCH_2), 6.71–7.33 (m, 18 H, ArH); ^{13}C NMR δ 20.52 ($ArCH_3$), 20.72 ($ArCH_3$), 20.79 ($ArCH_3$), 59.80 (OCH_3), 60.26 (OCH_3), 66.91 (OCH_2), 112.29, 127.04, 128.31, 128.72, 129.15, 129.62, 130.00, 130.34, 130.85, 131.10, 131.36, 131.73, 132.02, 132.26, 132.65, 134.47, 154.34, 154.46, 154.58; IR (KBr) 2930, 1600, 1500, 1465, 1415, 1235, 1020, 865, 805, 750; M^+, *m/e*, 798 (13), 797 (50), M^+ 796 (100), 779 (22), 778 (41), 765 (20), 764 (18), 749 (15), 692 (17), 105 (15). Anal. Calcd for $C_{54}H_{52}O_6$: C and H.

Methyl Transfers. 8. The Marcus Equation and Transfers between Arsenesulfonates

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Abstract: Using a ^{35}S label, rates of identity methyl-transfer reactions $XC_6H_4{}^*SO_3^- + CH_3O_3SC_6H_4X \rightarrow XC_6H_4{}^*SO_3CH_3 + XC_6H_4SO_3^-$ in sulfolane have been measured. For all five cases, these identity rates fit the Hammett equation with the rather large ρ of +0.6. Rates and equilibria for $XC_6H_5SO_3Me + 3,4\text{-}Cl_2C_6H_3SO_3^-$ have been measured. The fit to the Marcus equation using averages of the experimental identity rates for the intrinsic rate is perfect, within experimental error. The absolute values of ρ for the forward and reverse reactions differ by an amount quantitatively consistent with the nonzero identity reaction ρ. The significance of the identity reaction $\rho > 0$ is discussed.

Introduction

Rates of chemical reactions have been of interest for years, and it has long been recognized that, although thermodynamically unfavorable reactions are often very slow, there is no general correlation of rates with free-energy change. There are numerous examples of thermodynamically highly favorable reactions which are quite slow, such as the decomposition of TNT. After separating from these slow reactions those which mechanistically pass through highly unstable intermediates, many one-step slow reactions remain. A useful concept for such apparently anomalously slow reactions has been the Marcus equation,[1] which expresses the kinetic barrier as the sum of an intrinsic barrier and the thermodynamic barrier (together with higher order terms). The Marcus equation was initially designed for electron-transfer reactions in solution but later found application to hydrogen-atom transfers,[2] proton transfers,[3] and group transfers, especially methyl-transfer reactions.[4,5] eq 1. A form of the Marcus equation

$$\mathrm{Nu}_i\mathrm{Me}^a + \mathrm{Nu}_j^{\,b-1} \rightleftarrows \mathrm{Nu}_i^{\,a-1} + \mathrm{MeNu}_j^{\,b} \tag{1}$$

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(1) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

(2) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

(3) A review including the application of the Marcus equation to proton transfers is: Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475.

(4) (a) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87. (b) Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227.

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is eq 2,[6] where λ, the "intrinsic barrier", is taken as the average

$$\Delta G^{\ddagger}_{ij} = w^R + \lambda + \frac{\Delta G^\circ}{2} + \frac{\Delta G^{\circ 2}}{16\lambda} \tag{2}$$

of the barriers for the two identity reactions. The application to reactions without identity reactions is much more questionable,[4b,7] but these difficulties are not relevant to the present work. Equation 2 is not directly applicable to experiment since the values of w^R, λ, and ΔG° are not directly measurable.

Equation 2 can be converted to an experimentally useful form, if the following assumptions are made.

1. The work term, w^R, is structure independent throughout the series. Since w^R is largely made up of solvent–solute interactions, if the solvent is constant, and the charges *a* in eq 1 are all the same in the series studied as are the charges *b*, this is a reasonable assumption.

2. $w^R = w^P$, where w^P is the work term for the reverse reaction. In order to make this reasonable, the reverse reaction must be a member of the series of forward reactions; thus $a = b$. The reactions then belong to an isodesmic series. We may note here that the careful Menschutkin reaction work of Arnett and Reich[8] does not meet this criterion, and hence it is not surprising that the results are less simple. With this assumption the experimental free-energy change ΔG^0_{ij} is the same as that after overcoming w^R and before overcoming w_P. For that reason we do not introduce a new notation here.

The equations then can be rewritten, using the experimental identity free energies of activation. These are related to λ by

$$w^R + \lambda = {}^1/_2(\Delta G^{\ddagger}_{ii} + \Delta G^{\ddagger}_{jj}) \tag{3}$$

and the equation then becomes

$$\Delta G^{\ddagger}_{ij} = \frac{1}{2}(\Delta G^{\ddagger}_{ii} + \Delta G^{\ddagger}_{jj}) + \frac{\Delta G^0_{ij}}{2} + \frac{\Delta G^0{}_{ij}{}^2}{16[\frac{1}{2}(\Delta G^{\ddagger}_{ii} + \Delta G^{\ddagger}_{jj}) - w^R]} \tag{4}$$

Converting this to equilibrium and rate constant form (assuming $k = (RT/Nh)e^{-\Delta G^{\ddagger}/RT}$), we get

$$\ln k_{ij} = \frac{1}{2}(\ln k_{ii} + \ln k_{jj}) + \frac{\ln K_{ij}}{2} - \frac{(\ln K_{ij})^2}{16[\ln B - \frac{1}{2}(\ln k_{ii} + \ln k_{jj})]} \tag{5}$$

where $B = (RT/Nh)e^{-w^R/RT}$, i.e., the fictional rate constant for a reaction passing over a barrier of height w^R.

For many cases the quadratic term is negligible, and the equation remaining still has one feature attributable to Marcus: The two identity rates. If the identity rates and the equilibrium constants are measured, the calculated and experimental k_{ij} values can be compared. If this comparison is close, then extending to the point of large K_{ij} will allow next an evaluation of the need for a quadratic term, and with enough data, the possibility of evaluating *B* (i.e., w^R). This would constitute the most stringent test of the Marcus equation for methyl transfers. We may here note parenthetically that the inversion of relative reactivities of methyl iodide and dimethyl sulfate with the phenoxide and thiophenoxide nucleophiles[9] shows that the Marcus equation is not universally applicable.

In this paper we apply only the first of these tests for the case K_{ij} not far from unity, and provide the first available directly measured identity rates for methyl transfers in the case of $Nu^- = ArSO_3^-$.

Table I. Identity Rate Constants for Attack of Arenesulfonate Anions on Methyl Arenesulfonates in Sulfolane Solution

Ar in $ArSO_3^-$	$k_{35} \times 10^4$ [a]	$k_{45} \times 10^4$ [a]	$k_{55} \times 10^4$ [a]	$k_{65} \times 10^4$ [a]
p-$MeOC_6H_4$	0.162	0.463	1.2	
p-MeC_6H_4	0.20	0.60	1.54	
C_6H_5 [c]		0.66	1.7 [b]	4.9
p-ClC_6H_4		1.01	2.6	7.4
3,4-$Cl_2C_6H_4$		1.55	4.89	11.05

[a] All rate constants are in units of $M^{-1}\ s^{-1}$; the counterion was K^+ complexed by 18-crown-6. The subscripts refer to the temperatures, actually 35.0, 45.0, 55.0, and 65.0 °C. An error of ±5% in *k* is estimated. [b] Two significantly different results were obtained; the first, chronologically, while the technique was being developed was $k_{55} = 1.4 \times 10^{-4}\ M^{-1}\ s^{-1}$. The one in the table is considered more reliable. [c] In all runs with this substituted sulfonate, the radioactive label was initially in the ester. In all other cases the label was initially in the anion.

Table II. Rate and Equilibrium Constants for the Reaction of $ArSO_3CH_3$ with 3,4-Dichlorobenzenesulfonate Ion in Sulfolane at 55 °C

Ar	K_{eq}	k^+ [a] $\times 10^5$ $M^{-1}\ s^{-1}$	k^- [a] $\times 10^3$ $M^{-1}\ s^{-1}$
p-$MeOC_6H_4$	0.00308 (7)	1.16	3.76
p-MeC_6H_4	0.00514 (5)	2.03 [c]	3.94
C_6H_5	0.0147 (7)	3.51	2.39
p-ClC_6H_4	0.0880 (3)	9.98	1.13
3,4-$Cl_2C_6H_3$	1.00	48.9 [c]	0.489 [c]

[a] k^+ denotes the forward rate constant, k^- the reverse. [b] These numbers are not independent, for $K_{eq} = k^+/k^-$. [c] From Table I.

Table III. Hammett ρ Values for Rates and Equilibria

reaction	ρ [a]
$ArSO_3^- + MeO_3SAr$	+0.6 + 0.1
$ArSO_3Me + 3,4\text{-}Cl_2C_6H_3SO_3^-$ (k^+)	+1.83 + 0.14
(K_{eq})	+2.94 + 0.14
$ArSO_3^- + MeO_3SC_6H_3Cl_2$ (k^-)	−1.10 + 0.14

[a] The standard error in ρ is that calculated from the quality of fit of the line to the points; the identity of the last three is coincidental.

Results

Identity rate constants for reaction 6 were measured using a

$$\mathrm{Ar^*SO_3^- + MeO_3SAr \overset{k_{ii}}{\rightleftarrows} Ar^*SO_3Me + O_3SAr^-} \tag{6}$$

^{35}S label (usually in the sulfonate). From time to time the ester and the salt were separated by an extraction method and the ester was counted. The rate constants are given in Table I.

From Table I we find a value of ρ of 0.59 at 45 °C and 0.63 at 55 °C, which are not significantly different. The temperature dependence of ρ is without significance. Similarly, the variation in rates appears to arise mostly from the *A* factor rather than activation energy, but precision of the kinetics and the small temperature range renders this conclusion also insignificant. The results found are shown as E_a (kcal/mol), log *A* for the different substituents: p-OCH_3, 20.1 kcal/mol 9.5; p-CH_3, 20.6, 9.9; H, 21.1, 10.3; p-Cl, 21.1, 10.6; 3,4-Cl_2, 20.8, 10.4. Activation energies probably of somewhat lower precision for some unsymmetrical reactions of benzenesulfonate ion with 2-nitro-- and 2,3-chlorobenzenesulfonate are 20.4 and 22.0 kcal/mol, respectively.[10] The similarity suggests only that the results are not unreasonable.

The rates of reaction and equilibrium constants for the reaction of the methyl arenesulfonates with 3,4-dichlorobenzenesulfonate (as the 18-crown-6 potassium salt) were also measured, again using

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(5) Lewis, E. S.; Kukes, S.; Slater, C. D. *J. Am. Chem. Soc.* **1980**, *102*, 1619.

(6) Notation in the Marcus equation is highly variable. This one is a modification of that of Albery and Kreevoy,[4] in which the intrinsic barrier is λ (not Λ or λ/4). The free-energy change after the work term is overcome is simply ΔG°, since we later assume that it is the same as the experimental free-energy change. The subscripts *i* and *j* are used in conformity with reaction 1 in place of X and Y.

(7) Ritchie, C. D.; Kubisty, C.; Ting, G. Y. *J. Am. Chem. Soc.* **1983**, *105*, 279.

(8) Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1980**, *102*, 5892.

(9) Lewis, E. S.; Vanderpool, S. *J. Am. Chem. Soc.* **1978**, 100, 6421.

(10) Lewis, E. S.; Smith, M. J.; Christie, J. J. *J. Org. Chem.* **1983**, *48*, 2527.

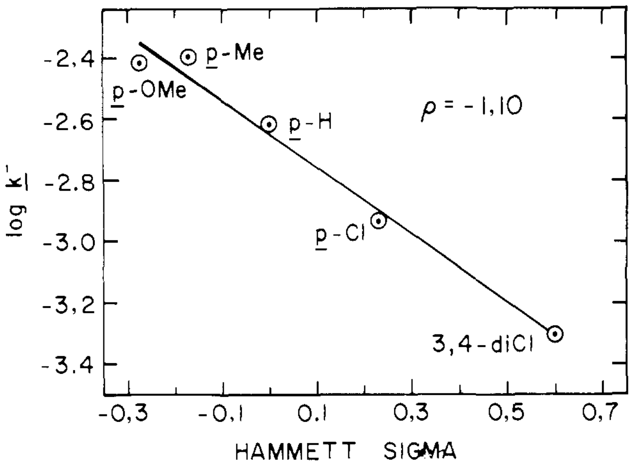

Figure 1. Hammett plot for the reaction rate of methyl 3,4-dichlorobenzenesulfonates with various arenesulfonate anions (k_{-1}).

the radioactive tracer followed by partition separation of salts from neutral esters, and counting of the latter. The results are presented in Table II.

Some preliminary rough equilibrium constants for the reactions of methyl *p*-toluenesulfonate with various sulfonate anions were measured by HPLC analysis of the ester mixture. Within a very large experimental error, there were no discrepancies; these results are not reported here.

Discussion

The substituents were chosen to allow the application of the Hammett equation, and Table III shows the ρ values found. Figure 1 shows the worst of the plots, for k^-, that is, the rate constant for arenesulfonate ions with methyl 3,4-dichlorobenzenesulfonate. The Hammett σ values used were:[11] *p*-OCH$_3$, -0.27; *p*-CH$_3$, -0.17; H, 0.00; *p*-Cl, $+0.23$; 3,4-Cl$_2$, $+0.60$; the last is the sum of meta and para σ values.

The ρ for k^-, -1.1 (at 55 °C, $k^-_{\mathrm{H}} = 2.4 \times 10^{-3}$ M^{-1} s^{-1}), i.e., the attack on methyl 3,4-dichlorobenzenesulfonate, on substituted benzenesulfonates and can be compared with Kevill's[12] value for the attack of methyl trifluoromethanesulfonate, methyl perchlorate, and trimethyloxonium ion on substituted benzenesulfonates. These ρ values are -1.06 (25 °C), -1.10 (0.3 °C), and -1.07 to -1.18 (-23.4 °C depending on ionic strength), respectively. The similarity of all these numbers is remarkable, even though the temperatures are different and the solvent in these last three is acetonitrile. The selectivity appears to be relatively constant over this wide range of reactivity (k_{25} for MeTf + PhSO$_3^-$ = 0.82 M^{-1} s^{-1}), a factor of more than 3000, allowing roughly for the temperature difference. The range of reactivity with virtually constant selectivity is wide, reminiscent of that observed with some amine nucleophiles.[13]

We can expect the nonidentity rates and equilibrium constants to obey the Hammett equation, as they indeed do. However, the identity rates, corresponding to a dual substitution, need not be expected to fit. The fact that they do shows that the surface defined by σ_i, σ_j, and log k is a plane, and that ρ for substitution in (for example) the nucleophile is independent of suustitution in the methyl esters.[14] Such a perfectly planar surface is considered impossible for a real dual substituent effect by Jencks and Jencks,[15] but, of course, our very small range of substituents is not likely to find any small curvatures, so no inconsistency really exists.

Before discussing quantitatively the significance of the numbers in Table III, it is worthwhile to consider the fact that these numbers are not independent. If we assume the Marcus equation (without the quadratic term)[16] as well as the Hammett equation, we can readily derive ρ for the forward reaction rate k^+:

$$\rho^+ = \tfrac{1}{2}\rho_{ii} + \tfrac{1}{2}\rho_{\mathrm{eq}} \tag{7}$$

and similarly for the reverse reaction (but with the equilibrium still written in the forward direction):

$$\rho^- = \tfrac{1}{2}\rho_{ii} - \tfrac{1}{2}\rho_{\mathrm{eq}} \tag{8}$$

Subtraction of these two relations gives the familiar relation for any equilibrium:

$$\rho^+ - \rho^- = \rho_{\mathrm{eq}} \tag{9}$$

which is totally independent of the Marcus expression, since it is readily derived from $k^+/k^- = K_{\mathrm{eq}}$. Clearly (except for a round-off value) this equation is obeyed by the values in Table III, as it must be.

Addition of (7) and (8) gives the less familiar relation:

$$\rho^+ + \rho^- = \rho_{ii} \tag{10}$$

which suggests an alternative determination of ρ_{ii}. In this case the experiments defining ρ_{ii} are different from those defining ρ^+ and ρ^-, and the application to the values in Table III constitutes a real test of the theory. From Table III, $\rho^+ + \rho^-$ is $+0.73$ (with an uncertainty of at least 0.1), in satisfactory agreement with the independent experimental value for ρ_{ii} of $+0.6$.

There are numerous alternative forms of this test, and the applicability of the Hammett equation is not necessarily required. An alternate approach of Albery and Kreevoy[4] is based on the observation that if a plot of log k^+ vs. log K_{eq} (i.e., a rate with i variable and j constant) (near log $K_{\mathrm{eq}} = 0$) is linear, one may differentiate the Marcus equation with respect to log K_{eq}, giving:

$$\frac{\mathrm{d}\log k^+}{\mathrm{d}\log K_{ij}} = \frac{1}{2}\frac{\mathrm{d}\log k_{ii}}{\mathrm{d}\log K_{ij}} + \frac{1}{2} \tag{11}$$

The slope of the plot thus differs by $^1/_2$ from the term $^1/_2$(d log k_{ii}/d log K_{ij}) which reduces in the Hammett case to $^1/_2(\rho_{ii}/\rho_{\mathrm{eq}})$, in this case $+0.10$. Thus the slope of the log k^+ vs. log K_{eq} is 0.60 instead of the 0.50 expected for a constant intrinsic barrier. The observed slope of this plot (made without reference to substituent effects on the identity rates) is 0.61.

There are very few published data allowing application of these results, which require substituent effects on reaction and equilibrium constants in a series including an identity reaction (or at least one of log $K = 0$). The case of hydride transfer between pyridinium ions of Kreevoy[17] is very relevant, and the discussion is parallel to this except that the Hammett equation is not used. One case is the methyl transfer between arylthiolates,[18] where the attack of PhSMe on ArS$^-$ was studied. The plot of log k^+ vs. log K_{eq} had a slope of 0.54; thus $\rho_{ii}/\rho_{\mathrm{eq}} = 0.08$ and with ρ_{eq} given as -3.80, ρ_{ii} becomes -0.30. In this case the uncertainties in ρ values are substantial and we may conclude only that ρ_{ii} (at 150 °C) is small and might be zero. The negative value is perhaps not well enough established to warrant extensive discussion, even though potentially of enormous interest.

Considerable interest attaches to the nonzero value of ρ_{ii} for these sulfonate reactions. First, the direct measurement as well as that derived from eq 10 assures us that the value is clearly and significantly nonzero and positive. There are three potential sources of a positive ρ value for these processes, which we shall discuss in increasing order of our interpretation of their contribution.

1. If the sulfonate salts are extensively ion-paired in solution, a positive ρ for the ion-pair dissociation constant is to be expected.

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(11) Fuchs, R.; Lewis, E. S. In "Investigations of Rates and Mechanisms of Reactions", 3rd ed., Part 1; Lewis E. S., Wiley-Interscience: New York, 1974; p 790.

(12) Kevill, D. N.; Lin, G. M. L. Bahari, M. S. *J. Chem. Soc., Perkin Trans. 2* **1981**, 49.

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(14) Miller, S. J. *J. Am. Chem. Soc.* **1959**, *81*, 101.

(15) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948.

(16) Common to a large number of theoretical or empirical rate-equilibrium relations, including several that may include identity rates.

(17) Kreevoy, M. M.; Lee, I-S. H. *J. Am. Chem. Soc.* **1984**, *106*, 2550. Manuscript kindly provided before publication.

(18) Lewis, E. S.; Kukes, S. *J. Am. Chem. Soc.* **1979**, *101*, 417.

Now, if the free anion is much more reactive than the ion pair and if ion-pairing is extensive, a positive ρ value will result. However, there is little reason to believe that ion-pairing is extensive. The points lie well on the Hammett plot, yet the maximum salt concentrations used were quite variable (H, 0.097 M; Cl, 0.027 M; Me, 0.06 M; OMe, 0.006 M; Cl_2, 0.005 M), and there is no evidence of a correlation of the calculated second-order rate constant with salt concentration. Furthermore, the complexation of the potassium ion by the crown ether is expected to be virtually complete, since there was an excess of this, and in similar solvents the association constants are about a million.[19] The association of most salts as ion pairs in methyl sulfolane and of 18-crown-6 potassium salts in similar solvents[20] is small or undetectable. We conclude that a significant and substitutent sensitive ion-pair association is not the source of the substantial positive ρ.

2. There may be an influence of the overall charge on ρ. Consider the reaction

$$XCH_3 + Y^- \underset{k}{\overset{k^+}{\rightleftarrows}} X^- + CH_3Y \tag{12}$$

in which X and Y are arenesulfonates and may be the same. If the transition state for a nearly symmetric case has the structure **1**, then we the effects of substitution in the two groups X and Y.

$$X^{-1/2}\cdots CH_3\cdots Y{-}^1/_2$$

1

In order to get a scale for these ρ values, we must also consider the reaction in which XCH_3 is completely converted to X^-, and that is conveniently the equilibrium ρ for variation in X with a constant Y ($\rho = +2.94$ in our case). For variation in X alone, we expect ρ to be −2.94 times the charge seen by X, which is not exactly $-^1/_2$, but is $-^1/_2[1 + (\mathrm{att}/2)]$, where the "att/2" is the charge on Y attenuated by the two dotted bonds. If these were ordinary bonds, we might estimate the attenuation as $(1/2.5)^2 = 0.16$, but this is almost certainly an overestimate. This would give ρ (for k^+ with constant Y), the ρ^+ of eq 11 $= +2.94[^1/_2 + (0.16/2)] = 1.70$. Similarly ρ^- (for attack of variable X^- on CH_3Y) should be $-2.94(^1/_2 - 0.08) = -1.23$, giving from eq 10, $\rho_{ii} = 1.70 - 1.23 = +0.47$.

This is almost certainly a considerable overestimate for ρ_{ii} for this case, and we may thus conclude that this electrostatic effect is a real contributor to ρ_{ii} but is insufficient to account for the observed result. It is of interest to consider this component of ρ for identity reactions of the form of eq 13. In this cationic case

$$X^+CH_3 + X \rightleftarrows X + CH_3{}^+X \tag{13}$$

the electrostatic effect is in the opposite direction. In one case a preliminary result[21] shows $\rho > 0$ for this identity reaction, suggesting that there is only a very minor contribution of the electrostatic effect, and we must therefore look elsewhere.

3. The most probable source of the substantial positive ρ is the contribution of the structure **2** to the transition state. This

$$X^-\overset{+}{C}H_3\overset{-}{X}$$

2

is a structure identified with the loose structure by Albery and Kreevoy, and its contribution is measured by their τ value. If the electrostatic term above is negligible, we may estimate the net charge on carbon, and hence the contribution of **2**, by using ρ to estimate the charge on the sulfonate. If **2** were the only contributing structure, then ρ_{ii} would be the same as ρ_{eq}, and the charge on carbon would be +1. The actual charge on carbon would then be $\rho_{ii}/\rho_{eq} = +0.20$. Because of the electrostatic effect (complicated by the partial + charge on carbon in **2**), the positive charge on carbon is probably somewhat less than this. This number corresponds to a value of $\tau = 0.8$ in Albery and Kreevoy's terminology.

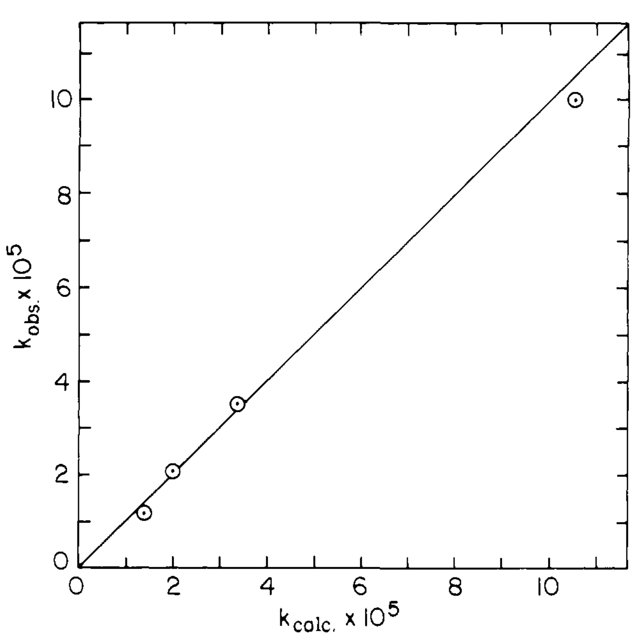

Figure 2. A plot of the observed rate constants for reaction of methyl arenesulfonates with 3,4-dichlorobenzenesulfonate ion against those calculated by $\log k_{ij} = {}^1/_2(\log k_{ii} + \log k_{jj}) + {}^1/_2K_{ij}$ using the data from Tables I and II. The line is that of unit slope. The point for methyl 2,4-dichlorobenzenesulfonate is not shown at $k_{obsd} = k_{calcd} = 48.9 \times 10^5$ $M^{-1}\,s^{-1}$ in order to have a reasonable scale; with this point the apparent curvature of the four points disappears.

Such determinations of ρ_{ii} appear to be the firmest measures of the contribution of structures such as **2**, and even provide an entry into measurement of possible structures with negative charge on CH_3, as postulated by Shaik,[22] which would lead to a negative ρ_{ii}. It is interesting that contributions of structures such as **3** might

$$X\cdot C\bar{H}_3\cdot X$$

3

be expected with X^- of low electron binding energy; perhaps the somewhat uncertain negative ρ_{ii} for the arylthiolates derived above is an example. Of course structures analogous to **3** but with a group being transferred of higher electron affinity than CH_3 such as phenacyl or *p*-nitrobenzyl or silyl would have an even better chance of bearing a negative charge in the transition state, and such identity reaction measurements will be very interesting. Kreevoy[17] calculates a substantial negative charge on the transferring hydride, giving him a slope of log *k* vs. log *K* of less than $^1/_2$.

Next, how well does the Marcus equation work, given these identity rates and equilibrium constants? Shown above was the success in understanding the slope of $\log k_{ij}$ vs. $\log K_{ij}$, but it is worthwhile to show directly the rate constant calculation. Over this small range the Marcus equation works very well indeed. Figure 2 shows a plot of the observed rate constants for methyl arenesulfonates with 3,4-dichlorobenzensulfonate ion, against those calculated by eq 5, neglecting the quadratic term.

If the estimation method of Albery and Kreevoy[4] for w^R is applied to sulfolane, $w^R \sim 1.5$ kcal/mol, and the quadratic term can be evaluated, and turns out to have an essentially negligible effect, amounting to an extreme correction of $-.20 \times 10^{-5}$ $M^{-1}\,s^{-1}$ for the rate constant calculated for the *p*-methoxy substituent, the extreme case. This term does indeed improve the fit of this point, but the average percent deviations using the quadratic are 9.8 vs. 7% for the linear form. Clearly we cannot use these data to evaluate w^R with any precision, nor even to show that any nonlinearity in the $\log k_{ij}$ vs. $\log K_{ij}$ is present.

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Finally, are the identity rates plausible? Since there are so few of these in the literature, it is not easy to compare, but one estimate for the unsubstituted case has been published, based upon a slope 0.5 extrapolation of rate and equilibrium data on ortho-substituted methyl benzenesulfonates with the unsubstituted benzenesulfonate.[10] That value is 2×10^{-5} M^{-1} s^{-} at 35 °C. Using the directly measured identity reaction rate constant measurements at 45, 55, and 65 °C, the rate at 35 °C is 2.1×10^{-5} M^{-1} s^{-1}, a number in unreasonably good agreement with the earlier estimate.

We cannot yet combine these results with earlier rate and equilibrium estimation of identity rates from the linear part of the Marcus measurements[23] to calculate many rates, for the methylsulfonates are not yet well placed on the equilibrium scale of that work.

We therefore conclude the following. (1) Identity rates and hence intrinsic barriers are by no means constant for methyl transfers even with rather similar leaving (and attacking) nucleophiles. (2) The reaction rates for methyl-transfer reactions with similar leaving and attacking groups are calculable from the intrinsic rates and the equilibrium constants with the Marcus equation. (3) The data do not allow a decision about the need for the quadratic term and the possible relation to the reactivity–selectivity principle.

Experimental Section

Materials. Sulfolane was purified as before.[24] The sulfonate esters were prepared from the commercially available sulfonyl chlorides with sodium methoxide in methanol.[10]

The substituted benzenesulfonates were isolated in yields of usually greater than 50%, even though purity was considered more important than yield. The structures were all demonstrated by NMR. The properties and criteria of purity are as follows: *p*-methoxy, bp 165 °C at 2.6 torr, single HPLC peak; *p*-methyl, bp 142 °C at 3.5 torr, no foreign peaks in NMR as much as 1% of major peaks; unsubstituted, bp 122 °C at 2.2 torr; *p*-chloro, mp 43 °C, assay 97.5% by base consumed on hydrolysis; 3,4-dichloro, mp 47–48 °C. Mass spectrum: calcd for $C_7H_6SO_3Cl_2$, 239.9414; found, 239.9414. This latter new compound was also prepared by the treatment of potassium 3,4-dichlorobenzenesulfonate with methyl trifluoromethanesulfonate in boiling ether for 1 h. Potassium sulfonates were made by sulfonation, neutralization, and separation from potassium sulfate by extraction in a Soxhlet extractor with ethanol, followed by recrystallization from ethanol. The ^{35}S-labeled sulfonic acids were made by sulfonation with a solution of active H_2SO_4 in fuming sulfuric acid. The yields are not large, since no excess sulfuric acid was used. The details of the individual sulfonations were as follows.

Potassium *p*-Methoxybenzenesulfonate-^{35}*S*. Fuming sulfuric acid (^{35}S labeled), 8.9 mL, was added to an equivalent amount of anisole, 16 mL, at −2 °C with stirring continued for 2 h. The reaction product was poured into ice and neutralized with 50% potassium hydroxide to an external litmus end point; the product solid was separated by filtration, dried at 130 °C, and combined with a further product obtained by five-fold concentration of the mother liquor. The dried solids were pulverized in a mortar, then put in the thimble of a Soxhlet extractor and extracted with ethanol; the extract was cooled to 3 °C and filtered yielding the potassium salt. The salt so obtained was recrystallized from ethanol. The NMR of the product in D_2O showed a clean aromatic quartet and no evidence of isomers, yield 16%, 7 mCi/mmol.

Potassium *p*-Toluenesulfonate-^{35}*S*. The procedure followed that of the *p*-methoxy derivative, except that a temperature of 40 °C was used for the sulfonation of toluene. The first salt isolated was contaminated with ortho isomer, but this was eliminated by recrystallization from methanol as shown by NMR in D_2O 3 Hs, δ 2.20, 4 H AB quartet, δ 7–8.0, $J = 9$ Hz), with no sign of the ortho isomer which gives the 3 Hs at δ 2.51; activity, 4 mCi/mmol.

Potassium *p*-chlorobenzenesulfonate-^{35}*S* was prepared as in the other cases, except that sulfonation of chlorobenzene was carried out at 55 °C.[25] No orthoisomer was observed by NMR in the aromatics region in the isolated products activity, 1.7 mCi/mmol.

Potassium 3,4-Dichlorobenzenesulfonate-^{35}*S*. Sulfonation of *o*-dichlorobenzene[26] was carried out as before except at 200 °C: activity, 4.4 mCi/mmol.

Methyl Benzenesulfonate-^{35}*S*. Since yields in sulfonation of benzene were entirely unsatisfactory, a sample of thiophenol-^{35}S (prepared by Mr. T. Douglas by the reaction of elemental sulfur with phenylmagnesium bromide) was oxidized with chlorine following the method of Douglas and Johnson[27] to benzenesulfonyl chloride, then converted to the methyl ester as in the other cases.

Identity Rates. A solution of a potassium sulfonate-^{35}S was prepared in sulfolane solution by long (ca. 12 h) stirring of a weighed amount with sulfolane containing 18-crown-6 in about 50% excess. After complete solution, the solutions were diluted to the mark in a 25-mL volumetric flask. The salt solution (10 mL) was added to a 25-mL volumetric flask which was then weighed, and then the corresponding methyl ester was added, and the flask again weighed. A few particles of calcium hydride were added, the contents as mixed, and a 1-mL aliquot was taken. The flask was then stoppered and placed in a thermostat (the temperature of which was referenced to a NBS-calibrated thermometer); other 1-mL samples were taken at appropriate times, including a last sample taken after reaction was virtually complete.

The 1-mL samples were added to 20 mL of water and 5 mL of ether and well mixed. The ether layer was separated and combined with three more ether extracts. The total (ca. 20 mL) ether extract was washed three times with water, the ether transferred quantitatively to a 50-mL flask, and the ether removed on the rotary evaporator. A dioxane counting solution was used to transfer the residue to a counting vial, and the solution in the vial was made up to 15 mL with more counting solution. The dioxane mixture was used since there was often a trace of water after removal of ether. The activity in the vials was then counted (Beckman scintillation counter with a counting precision of at least 1.5 and sometimes 0.7%).

All count rates were corrected for decay by extrapolating each one back to the same time. A plot of ln $|A_\infty - A_t|$ vs. time gave k_{obsd} as the slope (calculated by an unweighted least squares) and the second-order rate constant was calculated from $k = k_{obsd}/[(ArSO_3^-) + (ArSO_3Me)]$. Runs were generally done with a substantial excess of the unlabeled material to maximize the range of activity measured.

Other Rate and Equilibrium Measurements with Potassium 3,4-Dichlorobenzenesulfonate. Experiments followed the general scheme for the identity rates, except the salt was always potassium 3,4-dichlorobenzenesulfonate with a different ester in substantial excess. The equilibrium constant was calculated from the activity at "infinite" time and the initial concentrations; the rate constant was calculated from eq 14[28] for a reaction first order in the foward direction, second order in the reverse.

$$\ln \frac{A_0^2 - A_e A_t}{(A_t - A_e)(A_0)} = k\psi \frac{A_0 + A_e}{A_0 - A_e} t \tag{14}$$

In this case the activities at zero time (A_0), at equilibrium (A_e), and at time t (A_t) must be background corrected. The pseudo-first-order constants so obtained were converted to second-order constants by dividing by the initial excess ester concentration.

Control Experiments. 1. The sulfonate esters are stable in sulfolane at the temperatures used, as shown by the unaltered proton NMR of a concentrated solution of methyl benzenesulfonate after treating for 24 h at 120 °C.

2. The calcium hydride (used to scavenge water) is inert to the rest of the system, as shown by the unaltered spectra of methyl benzenesulfonate or potassium benzenesulfonate with 18-crown-6 in sulfolane with some solid calcium hydride held at 120 °C for 45 h.

3. Reproducibility of extraction and partitions. In one run four samples (at "infinite" time) were taken. Counting showed that these had the same counting rate within 1.5%.

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Registry No. *p*-$MeOC_6H_4SO_3^-K^+$, 10234-03-4; *p*-$MeC_6H_4SO_3^-K^+$, 16106-44-8; $PhSO_3^-K^+$, 934-55-4; *p*-$ClC_6H_4SO_3^-K^+$, 78135-07-6; 3,4-$Cl_2C_6H_3SO_3^-K^+$, 89690-47-1; *p*-$MeOC_6H_4SO_3Me$, 6214-19-3; *p*-$MeC_6H_4SO_3Me$, 80-48-8; $PhSO_3Me$, 80-18-2; *p*-$ClC_6H_4SO_3Me$, 15481-45-5; 3,4-$Cl_2C_6H_3SO_3Me$, 89690-48-2; CF_3SO_3Me, 333-27-7; *p*-$MeOC_6H_4{}^{35}SO_3^-K^+$, 89690-49-3; *p*-$MeC_6H_4{}^{35}SO_3^-K^+$, 89690-50-6; *p*-$ClC_6H_4{}^{35}SO_3^-K^+$, 89690-51-7; 3,4-$Cl_2C_6H_3{}^{35}SO_3^-K^+$, 89690-52-8; $Ph^{35}SO_3Me$, 89690-53-9; $H_2{}^{35}SO_4$, 13770-01-9; PhOMe, 100-66-3; *p*-$MeOC_6H_4{}^{35}SO_3H$, 89690-54-0; PhMe, 108-88-3; *o*-$MeC_6H_4{}^{35}SO_3^-K^+$, 89690-55-1; PhCl, 108-90-7; *o*-$Cl_2C_6H_4$, 95-50-1; $C_6H_5{}^{35}SH$, 71800-43-6; ^{35}S, 15117-53-0; PhBr, 108-86-1; $Ph^{35}SO_2Cl$, 89690-56-2.

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