g, 0.038 mol), DMF (125 mL), and 3,6,9,12,15-pentaoxahexadecyl tosylate (7.7 g, 0.019 mol) were added to a 250-mL flask. This mixture was stirred and heated (ca. 100 °C) for 48 h, cooled, and filtered, and the solvent was evaporated in vacuo. The residue was taken up in H_2O (100 mL) which was then washed with CH_2Cl_2 (2 × 100 mL). The CH_2Cl_2 was evaporated in vacuo. The residue was chromatographed (Al_2O_3, 0–1% 2-PrOH/hexanes) and distilled (Kugelrohr, 180 °C (0.05 torr)) to provide lariat ether **39** (2.5 g, 26%) as a colorless oil: ^1H NMR δ 2.82 (m, 6 H), 3.40 (s, 3 H), 3.65 (m, 38 H); ^{13}C NMR δ 54.58, 55.02, 58.83, 69.79, 69.91, 70.35, 70.49, 70.67, 71.86; IR 2880, 1450, 1350, 1120 cm^{-1}. Anal. Calcd for $C_{23}H_{47}NO_{10}$: C, 55.51; H, 9.52; N, 2.81. Found: C, 55.54; H, 9.80; N, 2.75.

Preparation of *N*-(Methoxypoly[ethyleneoxy(*n* ~8)]ethyl)monoaza-18-crown-6 (40). As described in procedure C polyethylene glycol monomethyl ether (average MW = 350, 24.5 g, 0.07 mol) was treated with *p*-toluenesulfonyl chloride (14.7 g, 0.077 mol) in pyridine (40 mL) to afford the tosylate (30.0 g, 85%). To a 50-mL round-bottomed flask, equipped with a magnetic stirrer and a reflux condenser, was added monoaza-18-crown-6 (**32**, 3.0 g, 0.0114 mol), Na_2CO_3 (1.2 g, 0.0114 mol), CH_3CN (10 mL), and the tosylate (5.8 g, 0.0114 mol). The reaction mixture was stirred at reflux for 24 h, cooled, and filtered, and the solvent was evaporated in vacuo. The residual oil was then chromatographed over a column of Al_2O_3 (5% 2-PrOH/hexanes) to give lariat ether **25** as a yellow oil (4.3 g, 60%): ^1H NMR δ 2.80 (m, 6 H), 3.40 (s, 3 H), 3.65 (m, 36 H). Anal. Calcd for $C_{29}H_{59}NO_{13}$: C, 55.31; H, 9.44; N, 2.22. Found: C, 55.46; H, 9.70; N, 2.30.

Preparation of *N*-(2-Methoxyphenyl)monoaza-18-crown-6 (41). Compound **41** was prepared as described above for **26** except that cyclization was effected with TEGMs (35 g, 0.1 mol). The crude mixture was chromatographed (Al_2O_3, 0–2% 2-PrOH/hexanes) and then distilled (Kugelrohr, 135 °C (0.02 torr)) to give the lariat ether **41** (15 g, 41%) as a pale yellow oil: ^1H NMR 3.65 (m, 27 H), 6.9 (m, 4 H); ^{13}C NMR δ 52.66, 55.16, 69.74, 70.24, 70.52, 70.70, 111.70, 120.12, 122.10, 139.35, 152.80; IR 3060, 2860, 1590, 1500, 1460, 1350, 1240, 1120, 750 cm^{-1}. Anal. Calcd for $C_{19}H_{31}NO_6$: C, 61.77; H, 8.46; N, 3.79. Found: C, 61.91; H, 8.75; N, 3.71.

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Registry No. 1, 41775-76-2; **2**, 84227-47-4; **3**, 90774-27-9; **4**, 96530-17-5; **5**, 90774-28-0; **6**, 96530-18-6; **7**, 96530-19-7; **8**, 90774-29-1; **9**, 80649-19-0; **10**, 98269-19-3; **11**, 96530-20-0; **12**, 98269-20-6; **13**, 96530-21-1; **14**, 66943-05-3; **15**, 69978-46-7; **16**, 69978-50-3; **17**, 69978-48-9; **18**, 98269-21-7; **19**, 71089-11-7; **20**, 79402-94-1; **21**, 79402-96-3; **22**, 80755-60-8; **23**, 80755-61-9; **24**, 80755-62-0; **25**, 82216-99-7; **26**, 98269-22-8; **27**, 98269-23-9; **28**, 98269-24-0; **29**, 85548-59-8; **30**, 88548-60-1; **31**, 98269-25-1; **32**, 33941-15-0; **33**, 69978-47-8; **34**, 63281-62-9; **35**, 79402-95-2; **36**, 80755-63-1; **37**, 80755-64-2; **38**, 80755-65-3; **39**, 80755-66-4; **40**, 82217-00-3; **41**, 98269-26-2; TEGTs, 37860-51-8; TrEGMs, 80322-82-3; TEGMs, 55400-73-2; TrEGTs, 19249-03-7; 2-$MeOC_6H_4N(CH_2COOEt)_2$, 98269-29-5; 4-$MeOC_6H_4N(CH_2COOEt)_2$, 98269-30-8; 2-$MeOC_6H_4CH_2N(CH_2COOEt)_2$, 98269-31-9; 1,11-diiodo-3,6,9-trioxaundecane, 36839-56-2; benzylamine, 100-46-9; 2-methoxyaniline, 90-04-0; 4-methoxyaniline, 104-94-9; (2-methoxybenzyl)amine, 6850-57-3; 2-nitrobenzyl chloride, 612-23-7; 3-amino-1-propanol, 156-87-6; *N*,*N*-dimethylethylenediamine, 108-00-9; 2-methoxyethylamine, 109-85-3; 3,6-dioxaheptyl tosylate, 50586-80-6; 3,6,9-trioxadecyl tosylate, 62921-74-8; 3,6,9,12-tetraoxatridecyl tosylate, 62921-76-0; 11-(allyloxy)-3,6,9-trioxaundecyl tosylate, 98269-27-3; allyl chloride, 107-05-1; diethanolamine, 111-42-2; *N*-allyldiethanolamine, 2424-05-7; *n*-butyl bromide, 109-65-9; *n*-butyldiethanolamine, 102-79-4; *N*-(*tert*-butyl)diethanolamine, 2160-93-2; benzyl chloride, 100-44-7; *N*-benzyldiethanolamine, 101-32-6; methoxyethanol, 109-86-4; 2-methoxyethyl tosylate, 17178-10-8; *N*-(3-oxabut-1-yl)diethanolamine, 79402-97-4; 2-(2-methoxyethoxy)ethanol, 111-77-3; *N*-(3,6-dioxahept-1-yl)diethanolamine, 79402-98-5; 3,6,9-trioxadecanol, 112-35-6; 3,6,9,12-tetraoxatridecanol, 23783-42-8; 3,6,9,12,15-pentaoxahexadecanol, 23778-52-1; 3,6,9,12,15-pentaoxahexadecyl tosylate, 80755-67-5; polyethylene glycol monomethyl ether, 9004-74-4; polyethylene glycol monomethyl ether tosylate, 58320-73-3; *N*-(methoxypoly[ethyleneoxy(*n*=8)]ethyl)diethanolamine, 98269-28-4; ethyl bromoacetate, 105-36-2; *N*-(2-methoxyphenyl)diethanolamine, 28005-76-7; *N*-(4-methoxyphenyl)diethanolamine, 19721-54-1; *N*-(2-methoxybenzyl)diethanolamine, 98269-32-0; 4-nitrobenzyl bromide, 100-11-8; *tert*-butyl chloroacetate, 107-59-5; chloroacetyl chloride, 79-04-9.

Methyl Transfers. 10. The Marcus Equation Application to Soft Nucleophiles

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Abstract: The Marcus equation applied to methyl transfers is shown to cover reactions of "soft" nucleophiles, although small discrepancies occur. Rates and equilibria are reported for a series of reactions of arylmethylselenides with (*p*-chlorophenyl)dimethylselenonium ion. Experimental reaction rates between "hard" methylating agents and "soft" nucleophiles show small deviations from the calculated values, mostly but not always in the direction predicted by the HSAB principle. The Marcus equation fails to explain the previously reported "inversion" of reaction rates of 4-nitrothiophenoxide and of 4-nitrophenoxide with methyl iodide and dimethyl sulfate. Identity rates for dimethyl sulfate, methyl methanesulfonate (using ^3He), methyl iodide (using ^{125}I), and methyl triflate (using ^{35}S) in sulfolane are reported.

The Marcus equation was developed to correlate electron-transfer reactions[1] and later found application to hydrogen atom transfers,[2] proton transfers,[3] and group transfers, especially methyl-transfer reactions.[4,5] The first critical evaluation of the Marcus equation is predicting methyl-transfer reactions, where identity reactions, equilibria, and cross reactions were directly measured, found the Marcus equation fitted the data within experimental error.[6] These reactions with oxygen leaving groups were transfers of methyl between various arenesulfonates.

Limitations on the application of the Marcus equation to group transfers might be found in those cases with participation of special transition-state interactions not present to the same extent in the identity reactions or in the ground states.

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Table I. Identity Rates for Methyl Transfers

methylating agent	T, °C	k_2 (±10%), M^{-1} s^{-1}
$MeOSO_3Me$	35	1.70×10^{-4} [a]
	55	1.14×10^{-3} [a]
	65	2.42×10^{-3} [a]
MeO_3SCH_3	35	1.22×10^{-2} [a]
MeI	15	0.61[a]
	30	1.85[a]
	35	(2.61)[b]
MeOTf	15	1.78×10^{-3} [a]
	35	1.32×10^{-2} [a]
$4\text{-}ClC_6H_4SeMe_2^+$	65	4.82×10^{-4} [c]
$4\text{-}MeOC_6H_4SO_3Me$	35	1.62×10^{-5} [d]

[a] This work by tracer exchange. [b] Calculated from data at 15 and 30 °C. [c] This work by LFER interpolation. [d] From ref 6.

Three "effects" which involve special transition-state interactions appeared to be possibilities, namely steric effects, hard–soft interactions, and the α effect. We originally studied methyl transfers in contrast to other group transfers in order to minimize steric effects, although they contribute both to the rates and equilibria even in methyl transfers.[7] No cases with obvious steric problems so far appear practical for either the measurements of identity rates or equilibria. The α effect, which constitutes a positive deviation from a linear plot of log k vs. pK_b for certain nucleophiles, is seldom big enough to be significant. In S_N2 reactions the largest reported α effect for methyl transfers is a factor of 8.8.[8]

The hard–soft acid–base principle[9] requires that for a thermoneutral reaction, the cross reaction for methyl transfer between a hard and a soft nucleophile must be slower than the averge of the two identity reactions, one with a favorable special transition-state hard–hard interaction and the other with a favorable soft–soft interaction. We have searched for hard–hard and soft–soft identity reactions of comparable rate; the closest we have here is about a factor of 100 between the rates. In this paper, we thus study cases with quite different identity rates and mostly far from thermoneutral.

In the search for other soft nucleophiles with measurable identity rates, we also describe some aryl methyl selenides as nucleophiles.

Results

Identity rate constants for reactions 1–4 were measured by following the decreasing radioactive tracer level in the salt (reactions 1 through 3) with time or by following the increasing tracer level in the methylating agent (reaction 4). These rate constants, together with a previously reported one, are given in Table I. An indirect synthesis of the ^{35}S-labeled (trifluoromethane)sulfonate (triflate) salts from $CF_3I + Na_2{}^3{}_5S$ is described in the experimental part.

$$I^{*-} + Me\text{–}I \rightleftarrows Me\text{–}I^* + I^- \quad (1)$$

$$^*H_3C\text{–}OSO_3^- + H_3C\text{–}OSO_3CH_3 \rightleftarrows {}^*H_3C\text{–}OSO_3CH_3 + H_3C\text{–}OSO_3^- \quad (2)$$

$$^*H_3C\text{–}SO_3^- + H_3CSO_3\text{–}CH_3 \rightleftarrows {}^*H_3CSO_3\text{–}CH_3 + H_3C\text{–}SO_3^- \quad (3)$$

$$F_3C^*SO_3^- + F_3CSO_3\text{–}CH_3 \rightleftarrows F_3C^*SO_3\text{–}CH_3 + F_3CSO_3^- \quad (4)$$

Table II. Reaction Rates for Reaction of 65 °C

$4\text{-}ClC_6H_4SeMe + ArSeMe_2^+ \rightarrow 4\text{-}ClC_6H_4SeMe_2^+ + ArSeMe$

substituent[a]	K_5	k_5,[e] M^{-1} s^{-1}	k_{-5}[b]
$4\text{-}CH_3O$	0.0324	8.80×10^{-5}	2.10×10^{-3}
$4\text{-}CH_3$	0.0901	1.42×10^{-4}	1.58×10^{-3}
$3\text{-}CH_3$	0.145	1.72×10^{-4}	1.19×10^{-3}
H	0.189	1.83×10^{-4}	1.00×10^{-3}
4-Cl	1.00[c]	4.82×10^{-4}	(4.82×10^{-4})[d]
4-CN	10.1	1.83×10^{-3}	1.82×10^{-4}
$4\text{-}NO_2$	24.8	2.58×10^{-3}	1.04×10^{-4}

[a] On phenyl group to make Ar. [b] Not statistically corrected. This was the usual direction in which most of the reactions were followed. [c] By definition. [d] Calculated from a plot of log k_{-5} vs. log K_{eq} at K_{eq} = 1. [e] Calculated from $K_5 = k_5/k_{-5}$.

Table III. Reactions between "Soft" and "Hard" Reagents

reactants	T, °C	k, M^{-1} s^{-1}	K_{eq}	k_{Marcus}
I^- + $4\text{-}CH_3OPhSO_3Me$	35	1.68×10^{-2}	38.5	4.0×10^{-2}
	45	4.57×10^{-3}	26.3	
I^- + CH_3SO_3Me	35	5.91×10^{-3}	37	3.4×10^{-2}
	45	1.59×10^{-2}	21.5	
4-ClPhSeMe + Me_2SO_4	65	1.48×10^{-4}	2.2	4.2×10^{-4}
I^- + MeOTf	35	3200	3.5×10^8	1500
I^- + $(MeO)_2SO_2$	15	0.20		
	35	1.0	1.62×10^4	2.58

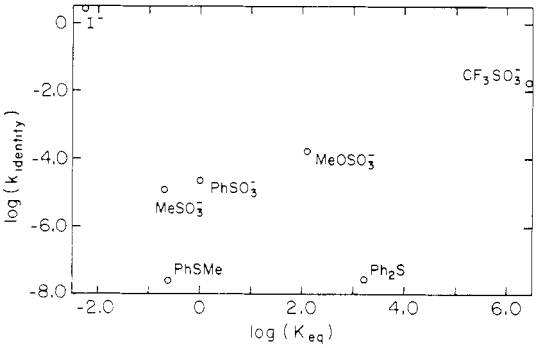

Figure 1. A plot of log $k_{identity}$ vs. log of the equilibrium constant for methyl transfer to benzenesulfonate,[10] at 35 °C. An unweighted least-squares line drawn through the sulfonate points has a slope of 0.45, which is significantly greater than the slope of 0.20 for a similar plot for arenesulfonates at 65 °C.[6,10]

A further identity rate was available from the measurement of rates and equilibria of a dimethyl(4-chlorophenyl)selenonium (trifluoromethane)sulfonate, followed by GC, eq 5. The results

$$4\text{-}ClPhSeCH_3 + ArSe(CH_3)_2^+ \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} 4\text{-}ClPhSe(CH_3)_2^+ + ArSeCH_3 \quad (5)$$

are shown in Table II. The identity rate constant of *p*-chlorophenyl methyl selenide was calculated from the log $K = 0$ intercept of a linear plot of log k_5 vs. log K_5 for reaction 5 with use of the rate and equilibrium data in Table II. The slope of this plot is 0.546; the Hammett plots have for the k_5, $\rho = 1.44$, for k_{-5}, $\rho = -1.20$, and for K_5, $\rho = 2.64$. The equilibrium constant for the reaction of methyl 4-chlorophenyl selenide with dimethyl sulfate was also measured, giving $K = 2.2$ at 65 °C in a solution a few hundredth molar in electrolytes. The equilibrium placement with the reference base[10] benzenesulfonate ion is roughly known, but it is not included here because of the temperature difference.

Several rate constants and equilibria for the reaction of iodide anion with a series of hard (i.e., sulfonate ester) methylating agents have been determined. These iodide–sulfonate cross-reaction rates are given in the second column of Table III. This table also gives

(7) The alkylation of pyridines by methyl iodide is retarded by 2-alkyl substituents. The dealkylation of methylpyridinium salts is accelerated by 2-alkyl substituents, both of these opposite to the effect of 4-alkyl substituents. Berg, U.; Gallo, R.; Metzger, J. *J. Org. Chem.* **1976**, *41*, 2621. Berg, U.; Gallo, R.; Metzger, J.; Chanon, M. *J. Am. Chem. Soc.* **1976**, *98*, 1260. Similar effects are seen with 2-chloropyridine. Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1980**, *102*, 5892.

(8) The α-effect appears to be small in methyl transfer reactions. (a) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B.; Minot, C.; Eisenstein, O, *Tetrahedron Lett.* **1982**, 615. The largest reported α-effect for a methyl transfer reaction is k_{HOO^-}/k_{MeO^-} with methyl (*p*-nitrophenyl)sulfate = 8.8 ± 2.2. (b) Buncel, E.; Chuaqui, C.; Wilson, H. *Int. J. Chem. Kinat.* **1982**, *14*, 823.

(9) (a) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827. Symbiotic effects are found. (b) Pearson, R. G.; Songstad, J. *J. Org. Chem.* **1967**, *32*, 2899.

(10) Lewis, E. S.; Douglas, T. A.; McLaughlin, M. L. *Isr. J. Chem.*, in press.

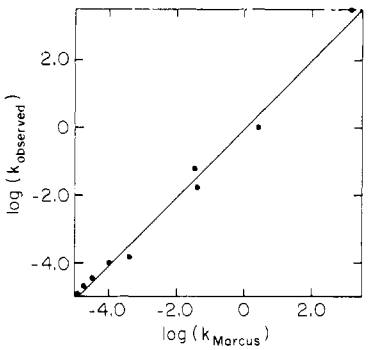

Figure 2. A plot of the log of the rate constant calculated by the Marcus equation vs. the log of the observed rate for reactions in Table III. Included as well are points for the reactions of various methyl arenesulfonates with (3,4-dichlorobenzene)sulfonate at 55 °C.[6] The line is an unweighted least-squares fit with a slope of 1.016.

the rate constant for 4-chlorophenyl methyl selenide with dimethyl sulfate. All reactions were carried out in sulfolane (tetrahydrothiophene 1,1-dioxide).

Discussion

The identity rates are of interest in themselves for several reasons. Methyl iodide is the weakest methylating agent of those reported here, yet its identity rate is several orders of magnitude faster than any of the sulfonate identity rates. This is in contrast with the experimental results found among the arenesulfonates. In those experiments,[6] the identity rate is slower when the equilibrium methylating strength is weaker. A logarithmic plot of identity rates vs. equilibrium constant for reaction with benzenesulfonate ion at 35 °C is shown in Figure 1. It is clear that the very poor correlation shown earlier[5] is substantiated by the direct measurements. Also, the rather good correlation with only sulfonates confirms the small-range results with arenesulfonates.[6]

In connection with the hard–soft acid–base principle, the high identity rate of the iodide identity methyl transfer is perhaps a conspicuous example of the "soft–soft" interaction. The fast methyl iodide identity rate is also in conformity with the well-known idea that iodide, more than any other familiar nucleophile, is both a "good" leaving group and a "good" nucleophile.

The data in Table II on the selenonium salts as methylating agents allow us to determine the substituent effect on the identity reaction for this case as $\rho_+ + \rho_- = \rho_{ident} = +0.24$. Similarly, an estimate of the charge on the transferring methyl group in the identity reaction (and on the other reactions in the table) of $\rho_{ident}/\rho_{eq} = 0.091$ fraction of an electron charge can be made. This number is significantly smaller than that calculated for the methyl transfers between arenesulfonates ($\rho_{ident}/\rho_{eq} = 0.20$),[6] and some of the difference can be attributed to the electrostatic factor discussed in the earlier work. However, the lesser electronegativity of selenium compared to oxygen probably also contributes.

The identity rates for methyl transfers between aryl methyl selenides are much faster (a factor of ca. 10^3) than that between two phenyl methyl sulfides, for which the value (at 65 °C) 4×10^{-7} has been reported.[5] This appears to be consistent with the idea that the unusual behavior of iodide is related to its high atomic number and that going down the periodic table should make a group both more nucleophilic and a better leaving group. Indeed this expectation led us to study the selenium compounds in the first place.

The rates of the unsymmetrical reactions with "soft" nucleophiles and "hard" leaving groups are given in Table III, which shows in the last column the rate calculated by the Marcus equation (assuming $w^R = -w^P = 1.5$ kcal/mol).[6] The experimental results in all but one case are smaller than the calculated result, in conformity with the expectation from the HSAB principle. However, the deviations are remarkably small, and the more striking result is that the calculations by the Marcus equation are so close. Figure 2 shows a logarithmic plot of the calculated vs. observed rates now covering more than a factor of 10^8 in rate. The least-squares line drawn has a slope of 1.016, clearly indistinguishable from a slope of 1 for agreement without any trend. The contribution of the Marcus quadratic term, while perceptible, is not in any case a major component of the calculated rate. Thus, the agreement with the Marcus equation within experimental error of the rather narrow range of methyl transfers between arenesulfonates[6] is now considerably extended with little loss of precision, and in these experiments, any special transition-state interactions are absent or inconspicuous.

Results which seem to show some "soft–soft" and "hard–hard" effects have been reported for other reactions. For *p*-nitrophenoxide, the ratio of the rate with methyl iodide to the rate with dimethyl sulfate was 0.12, while for 4-nitrothiophenoxide, the same rate ratio is 7.5.[11] It would be desirable if such "inversions of reaction rates" would be predicted by the Marcus equation. However, since the identity rates for *p*-nitrophenoxide and *p*-nitrothiophenoxide are extremely small (the number for thiophenoxide in ethanol at 35 °C is calculated by using Arrhenius extrapolation over more than 100 °C to be 4×10^{-12} M^{-1} s^{-1}),[10] such numbers cannot be realistically measured.

Yet one can still make some quantitative analysis of the Marcus equation in these cases as follows. It can be relatively easily shown that if one uses only the linear terms of the Marcus equation, eq 6, the rate ratio for two different methylating agents (represented

$$\ln k_{XY} = \tfrac{1}{2}(\ln k_{XY} + \ln K_{YY}) + \tfrac{1}{2} \ln K_{XY} \qquad (6)$$

as X and Z) reacting with the same nucleophile (represented as Y) is given by eq 7; it is a constant which depends upon the rate ratio of their identity reactions and upon their relative equilibrium methylating power but is independent of the nature of the nucleophile Y:

$$\ln (k_X/k_Z)_Y = \tfrac{1}{2}[\ln (k_{XX}/k_{ZZ}) + \ln K_XZ] \qquad (7)$$

With use of the identity rates in this paper and the relative equilibrium methylating power of methyl iodide (X) and dimethyl sulfate (Z),[10] $\ln (k_X/k_Z)_Y = -0.025$, a rate ratio of 0.98.

This ratio does not exactly predict the experimental rate ratios, although the two methylating agents are usually close in rate. The cases of the phenoxides and thiophenoxides have large but unknown equilibrium constants, so that the quadratic term of the Marcus equation perhaps should not be neglected. For this reason, the quadratic terms are included in the following analysis.

The two quadratic Marcus equations for the reactions of methyl iodide and dimethyl sulfate with 4-nitrophenoxide have three unknowns: the identity rate for 4-nitrophenoxide and its relative equilibrium methylating power to each of the methylating agents. Since the relative equilibrium methylating power of the two methylating agents is known, the latter two unknowns are actually one unknown. If the two equations are expanded and subtracted from each other, a linear equation relating the 4-nitrophenoxide identity rate to its equilibrium methylating power is obtained. Substituting this into one of the original equations, a quadratic equation for its equilibrium methylating power is produced. The two solutions to the initial equations, using all of the available data, are the following: $\ln K_{XY} = -25.1992$, $\ln k_{YY} = 25.474$ and $\ln K_{XY} = 1388.85$, $\ln k_{YY} = -466.776$. Clearly, the first solution is impossible. The second solution at least has $\log K > 0$ and is not absolutely impossible, but it is unbelievable, and it falls far outside of the valid range of the Marcus equation. A similar calculation for the thiophenoxide case gives equally nonsensical results. This lack of credible results indicates that we are at a situation where even the quadratic terms cannot explain the inversions.

The failure to find a plausible solution suggests that the quadratic term required to get a solution is insignificant, a conclusion previously reached from the observation that the reactivity–selectivity principle did not seem to be obeyed in these methyl transfers.[11] Thus, we can only find the product of the nitrophenoxide (or thiophenoxide) identity rate constant and its equilibrium constant with the methylating agents, i.e., $k_{YY}K_{XY}$.

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

Thus the inversion of reactivity of dimethyl sulfate and methyl iodide between the oxygen and sulfur nucleophile is not currently explicable by the simplified Marcus equation, and within the more general Marcus equation it can only be explained by substantial variation in the work terms. The observation that dimethyl sulfate reacts faster than methyl iodide with first-row nucleophiles but slower with nucleophiles in second or later rows appears to be general.[12]

The identity exchange, which we assume passes through an ordinary S_N2 mechanism, might also be accomplished by a sort of S_N1 mechanism. Although we reject CH_3^+ as a viable solution intermediate, the O-methylated sulfolane (**1**) is a plausible species and is a rather specifically solvated methyl cation. Jackman and co-workers[13] have observed this species, and in this laboratory we have observed both this ion as a transient intermediate (from CH_3OSO^+ + sulfolane) and the analogous but more stable O-methylated dimethyl sulfone.[14] The instability of methyl triflate in sulfolane at 170 °C was attributed to the decomposition of the species formed to a small extent by reaction 8.[5] If the forward rate of (8) is significant, then this (together with the presumably

$$\mathrm{MeOTf} + \mathrm{C_4H_8SO_2} \rightleftharpoons \mathrm{C_4H_8SO_2Me^+} + \mathrm{OTf^-} \qquad (8)$$

very rapid exchange of the triflate produced with labeled triflate in solution) constitutes an exchange mechanism, with the rate-determining step independent of the triflate ion concentration. An experiment to determine the order of the exchange in triflate finds that by using a tenth of the concentration of triflate, i.e., about 10^{-3} M (with about 10 times the specific activity, so that adequate counting levels could be achieved), the apparent second-order identity rate constant is 1.3×10^{-2} M^{-1} s^{-1}. thus the contribution of eq 8 to the exchange can be calculated, and the corrected S_N2 rate constant is still effectively 1.2×10^{-2} M^{-1} s^{-1}. The probably very small rate constant for reaction 8 is not reliably determined from this result. The rate constant for reaction 4 can be compared to the estimated rate of 4×10^{-4} M^{-1} s^{-1} from a correlation of identity rates with equilibrium methylating power[10] and the considerably higher early value 6.6×10^{-2} estimated with considerable cumulative error from unsymmetrical rates and equilibrium constants.[5]

Another question which arises from a consideration of reaction 8 is the possibility that the actual reagent in the reaction of iodide ion with methyl triflate is **1**. The unexpectedly high rate of this reaction leads to this suspicion. At first sight, the rate constant is far faster than any upper limit for the rate constant of reaction 8, excluding this possibility. However, the experimental design with a large excess of methyl triflate allows the possibility that **1** was formed slowly before the reaction was started. Thus, the equilibrium amount of **1**, formed slowly, was still enough in excess of the amount of iodide (10^{-3} to 10^{-2} M) to simulate a pseudo-first-order reaction course. This equilibrium concentration of **1** would be a larger fraction of the total methyl triflate concentration in the most dilute solutions; thus the reaction, instead of being first order in MeOTf, would be half-order. Experimentally a half-order reaction is excluded as the sole contribution, but a small contribution of a half-order reaction is not.

We have attempted to determine the equilibrium constant for methylation of sulfolane by methyl triflate by looking for the triflate anion by ^{19}F NMR. The triflate ion is clearly present in dilute solutions of the methyl ester, but the amount increases with time. Apparently there is a fairly rapid reaction with adventitious nucleophiles (probably water) which uses up about 10^{-2} M triflate. There is a further slow reaction which may be irrelevant to any reasonably fast reactions. The initial triflate ion concentration nevertheless gives an upper limit to the equilibrium constant ($K_8 = (MeO_2^+SC_4H_8)(OTf^-)/(MeOTf)$) of about 10^{-4} M. However, we have no evidence for any real ^{19}F NMR detectable equilibrium amount of triflate. The same upper limit is set by the observations of Jackman;[13] the largest equilibrium constant in his list is about 10^4 times that of methyl triflate. Since a stronger methylating agent than **1** cannot be measured in sulfolane because of a "leveling" effect, **1** must not be less powerful than anything in that list.

The slow reaction mentioned above converts about half of the triflate in sulfolane to triflate ion (presumably triflic acid) in about 36 h, which (if the previously proposed decomposition mechanism, reaction 9, is correct) corresponds to a value of k_9K_8 of 5×10^{-6} s^{-1} at room temperature. Thus solutions of 0.1 M MeOTf in

$$\mathbf{1} + \mathrm{OTf^-} \xrightarrow{k_9} \text{product} + \mathrm{H^+} + \mathrm{OTf^-} \qquad (9)$$

sulfolane 10 min after mixing (an estimate of the minimum time to get stopped flow kinetics) will contain ca. 3×10^{-4} M triflate ion. This amount will clearly substantively suppress the extent of reaction 8 if the equilibrium constant K_8 is 10^{-6} or less. There is an analogy to possible methylation by **1** in equilibrium with methyl triflate to the detection of general acid catalysis in water with unbuffered solutions. Although the equilibrium concentration of **1** may be small, **1** is presumably a faster methylating agent than methyl triflate. If we apply the Marcus equation assuming a constant intrinsic barrier, and no quadratic term, these two factors exactly compensate, and the contribution of the two methylating agents will be equal as long as no excess triflate ion is added, and as long as the equilibrium is maintained. In a dilute solution of the weak acid HX in water, the contribution of catalysis by H_3O^+ and HX will be equal (assuming $\alpha = 0.5$) as long as no X^- is added. The major distinction is that equilibrium in the acid catalysis case is indeed rapidly established, but the equilibrium between **1** and methyl triflate may be more slowly established and might limit the rate of methylation by **1**. We conclude that reaction 8 is irrelevant from the observations that (1) methylation of iodide by methyl triflate is first order in methyl triflate, (2) the "identity reaction" second-order rate constant does not have an important first-order component, and (3) the time-dependent triflate ion formation does not seem to introduce kinetic uncertainties.

Experimental Section

Materials. Sulfolane was purified as before.[15] Dimethyl sulfone was recrystallized from water and dried in vacuo. Sodium iodide was ground to a fine powder and dried at 140 °C. Tetrabutylammonium iodide was dried in vacuo to a constant weight. The bis(triphenylphosphoranylidene)ammonium (PPN) salts were prepared according to a literature procedure.[16] Dimethyl sulfate and the sulfonate esters were distilled from calcium hydride at reduced pressure and stored under nitrogen. Methyl iodide was freshly distilled from calcium hydride.

Dimethyl Sulfate-^3H. The labeled dimethyl sulfate used throughout was prepared from 15 μL of a carrier-free benzene solution of dimethyl sulfate (Amersham) 1 mCi/mL diluted into 100 mL of freshly distilled dimethyl sulfate.

PPN Methyl Sulfate-^3H. $(PPN)SO_4$, 5.30 g (4.52 mmol), was dissolved in a minimum of hot acetone (200 mL). A 20% excess of labeled dimethyl sulfate (0.50 mL) was added all at once, and the solution was refluxed for 1 hour. Ether was added to the warm solution until a permanent precipitate formed in the stirred mixture. Crystallization of the PPN methyl sulfate was complete after 10 h at room temperature. The white crystals were collected and dried in vacuo to give 5.10 g or 87% yield: NMR ($DCCl_3$) δ 7.3–7.8 (m, 30), 3.74 (s, 3); mp and mixture mp 206–207.5 °C, with an authentic sample. The same procedure was followed starting with ^{35}S labeled dimethyl sulfate.

PPM Methanesulfonate-^3H. Sodium iodide, 15.0 g (0.1 mol), was partially dissolved in 25 mL of sulfolane and treated with 9.2 mL (0.12 mol) of labeled dimethyl sulfate. The mixture was stirred for 20 min and 11.4 g (80.3 mmol) of methyl iodide was distilled out of solution. The methyl iodide was treated with 10.0 g (79.4 mmol) of sodium sulfite dissolved in a minimum of water and refluxed for 3 h. The solvent was removed in vacuo. The residue was suspended in hot acetone and treated with 8.7 g (74 mmol) of inactive sodium methanesulfonate. The volatiles were allowed to boil off. The PPN salt was prepared according to ref 16. The properties ^1H NMR ($DCCl_3$) δ 7.3–7.8 (m, 30), 2.77 (s, 3) and

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the mp 219–220 °C agreed with data obtained from the unlabeled salt.

Grignard Method for Aryl Methyl Selenide. The literature procedure[17] to prepare selenophenol was followed on a fourth of the reported scale. The workup was modified to include the addition of 8 mL of MeI in 20 mL of ether followed by a 30-min reflux. Then dilute HCl was added until the aqueous layer remained acidic and the remainder of workup was followed as reported. The isolated yields were consistently 55–65%. **Phenyl Methyl Selenide**: ^{1}H NMR ($DCCl_3$) δ 7.1–7.4 (m, 5), 2.35 (s, 3); bp 43–47 °C (0.5 mmHg). **Methyl *p*-Tolyl Selenide**: ^{1}H NMR ($DCCl_3$) δ 7.0–7.4 (m, 4), 2.30 (s, 6); bp 42–43 °C (0.1 mmHg). **Methyl *m*-Tolyl Selenide**: ^{1}H NMR ($DCCl_3$) δ 6.9–7.3 (m, 4), 2.28 (s, 6); bp 44 °C (0.1 mmHg). **4-Methoxyphenyl Methyl Selenide**: ^{1}H NMR ($DCCl_3$) δ 6.7–7.8 (m, 4), 3.76 (s, 3), 2.28 (s, 3); bp 62–63 °C (0.08 mmHg). **4-Chlorophenyl Methyl Selenide**: ^{1}H NMR ($DCCl_3$) δ 7.2–7.4 (m, 4), 2.36 (s, 3); bp 64–65 °C (0.12 mmHg); mp 28 °C.

Diazonium Salt Reaction with Selenocyanate Anion. The 4-nitro- and 4-cyanoanilines were diazotized and treated with potassium selenocyanide. The aryl selenocyanates were hydrolyzed and methylated following a literature preparation of the nitro derivative.[18] **Methyl 4-Nitrophenyl Selenide**: ^{1}H NMR ($DCCl_3$) δ 7.3–7.8 (m, 4), 2.45 (s, 3); mp 55.5–56.5 °C. **4-Cyanophenyl Methyl Selenide**: ^{1}H NMR ($DCCl_3$) δ 7.3–8.3 (br, 4), 2.40 (s, 3); mp 45 °C; Anal. Calcd for C_8H_7NSe: mol wt 196.9744. Found: 196.9746.

Methyl Iodide Identity Rate. A labeled NaI solution was prepared from 100 mL of a eutectic mixture of sulfolane/dimethyl sulfone[19] to make a 6.892×10^{-3} M NaI stock solution which was charged with 1.0 μL of a $Na^{125}I$ solution. A fresh solution of MeI was prepared for each run, close to the concentration of the salt. Twenty milliliters of each solution were thermostated to the appropriate temperature and added to a flask to give concentrations in the range of $3–4 \times 10^{-3}$ M for each. Then a 2.00-mL sample was taken, partitioned between 4 mL of water/20 mL of CCl_4, and maintained in an ice bath until the aqueous layer could be separated. The aqueous solution (3.00 mL) was counted with a precision of at least 1.5% in a Beckman γ counter.

A plot of $\ln |A_{inf} - A_t|$ vs. time gave k_{obsd} as the slope by unweighted least squares. The second-order rate constant was calculated from $k_2 = k_{obsd}/([NaI]_0 + [MeI]_0)$.

Rate and Equilibrium Measurements between MeO_3SMe and *p*-$MeOPhSO_3Me$ with Iodide. Experiments followed the general scheme for the iodide identity rate except that tetrabutylammonium iodide was used. The equilibrium was calculated from the activity after 7 half-lives of the reaction and the initial concentrations. The rate constant was calculated by using the equation for second-order reversible reactions in Frost and Pearson.[20] The activities were corrected for background.

Dimethyl Sulfate Identity Rates. A 50-mL sulfolane solution of 0.9256 g (0.002849 M) of PPN $O_3{}^{35}SOMe$ and 1.8943 g (0.30037 M) of dimethyl sulfate was prepared at room temperature. A 5-mL aliquot was withdrawn as the zero point, the flask was immersed in a bath, and 5-mL aliquots were taken at various times. The samples were dissolved in 3 volumes (15 mL) of acetone and 200 mL of ether. The salt crystallized after 48 h at −14 °C. The crystals were dried and weighed in tared scintillation vials. A toluene scintillation counting solution with 5% methanol by volume as a solubilizing agent was used with a Beckman scintillation counter. The rate constant was obtained from the raw data as in the iodide identity rate.

Methyl Methanesulfonate Identity Rate. The procedure was the same as in the dimethyl sulfate identity except that the initial solution was separated into 5-mL samples and sealed in ampules to protect against adsorbed water or air over the course of the longer reaction times. Also, 400 mL of ether was necessary to effect crystallization of the PPN salt.

Aryldimethylselenonium Rate and Equilibrium Measurements. With use of a sulfolane stock solution containing an internal standard, dibromobenzene, or tri(*tert*-butyl)benzene, an amount of aryldimethylselenonium triflate was dissolved in about 9 mL such that in a 10.00 mL volume its concentration would be near 0.1 M. The desired aryl methyl selenide was added at room temperature, and the solution was diluted with the sulfolane stock solution to volume. The (4-chlorophenyl)dimethylselenonium triflate was treated with X-PhSeMe where X = 4-MeO, 4-Me, 3-Me, and H. The 4-chlorophenyl methyl selenide was treated with X-PhSe(Me)$_2O_3SCF_3$ where X = 4-NO_2 and 4-CN. A 0.50-mL aliquot was taken and partitioned between 1.0 mL of tetrachloroethylene/10 mL of water as the zero point and the flask was placed in a 65 °C bath. After one extraction there was no sulfolane or salt left in the organic phase and, using GC analysis, the reproducibility was at least 1.0%. The GC analyses were performed on a Varian series 1400 GC, equipped with a 4 m × $^1/_8$ in. o.d. column with 5% SE-30 on Chromosorb W at column temperatures ranging from 120 to 170 °C. The peak areas were integrated with a Hewlett-Packard 3390A integrator. The ratio of internal standard to the decreasing selenide concentration was used to calculate a second-order rate constant with use of the same equation as that for the iodide/sulfonate rates. The equilibrium constant was calculated from the concentrations after at least 7 half-lives and the known initial concentration of the starting selenide.

Rate and Equilibrium Measurements for the Reaction of Dimethyl Sulfate with 4-Chlorophenyl Methyl Selenide. The procedure for the rate measurement was the same as that with the selenonium–selenide reactions above. The concentrations of the reactants were in the range of 9–40 mM in each. The equilibrium constant obtained by GC analysis of the mixtures after 7 half-lives agreed within experimental error with that obtained by ^{1}H NMR. The equilibrium concentrations were measured by peak area integration of the dimethyl sulfate δ 3.9 and methyl sulfate anion δ 3.5 in sulfolane-d_4.[21]

Rate Measurements of the Reaction of Dimethyl Sulfate and Iodide. Stock solutions of dimethyl sulfate and tetra(*n*-butyl)ammonium iodide with an internal standard of 1,2-dichloroethane were made, using a eutectic mixture of dimethyl sulfone and sulfolane as solvent. Concentrations were measured in weight percent and densities were taken. Both solutions were cooled to the desired reaction temperature. A weighed amount of the iodide solution was added to the nitrogen-purged water-jacketed addition funnel. The reaction was initiated by adding a weighed amount of the dimethyl sulfate soluton. Timed points were taken by rapidly mixing a sample (0.5–2 mL) with a 1:10 (v/v) tetrachloroethylene:water mixture which had been chilled in an ice bath. The organic layer was separated and kept in an ice bath until GC analysis for CH_3I was perfomed as above (the GC was held at room temperature). A second-order plot was made and the rate constant determined. Initial concentrations were calculated by determining the volumes of the stock solution which had been used and the weights of the reagents used. The volumes were assumed to be additive and the initial concentratins were determined, in the range of $1–5 \times 10^{-3}$ M. The reactions were run at both 15 and 35 °C with good reproducibility.

General Procedure for the Preparation of Aryldimethylselenonium Triflates. The X-PhSeMe (8.0 mmol), where X = 4-Cl, 4-CN, and 4-NO_2, is dissolved in 20 mL of dichloromethane and treated with a 20% excess (9.6 mmol) of methyl triflate. The stirred solution is warmed until the heat of reaction alone refluxes the solvent. After the mixture is cooled to room temperature the precipitate is collected and dried in vacuo. Yield 85–96%. **(4-Chlorophenyl)dimethylselenonium Triflate**: mp 122–123 °C; ^{1}H NMR ($DCCl_3$) δ 7.66–8.2 (m, 4), 3.32 (s, 6). Anal. for $C_9H_{10}ClF_3O_3SSe$—Theory: C, 29.24; H, 2.73. Found: C, 29.03; H, 2.71. **(4-Cyanophenyl)dimethylselenonium Triflate**: mp 132–133 °C; ^{1}H NMR ($DCCl_3$) δ 8.0–8.44 (m, 4), 3.38 (s, 6). Anal. for $C_{10}H_{10}F_3NO_3SSe$—Theory: C, 33.34; H, 2.80. Found: C, 33.24; H, 2.80. **(4-Nitrophenyl)dimethylselenonium Triflate**: mp 124–125 °C; ^{1}H NMR ($DCCl_3$) δ 8.45 (s, 4), 3.41 (s, 6). Anal. for $C_9H_{10}F_3NO_5SSe$—Theory: C, 28.43; H, 2.65. Found: C, 28.44; H, 2.72.

Benzyl Mercaptan-^{35}S.[22] A round-bottom flask equipped with a dry ice condenser and a stirring bar is charged with 12.9 g (53.7 mmol) of $Na_2S \cdot 9H_2O$ and 180 mL of absolute ethanol. A condensed volume of H_2S to equal 1.83 g (53.6 mmol) was distilled into the reaction through a cannula and the mixture was stirred for 15 min. The dry ice condenser was removed and 1.0 mg of $Na_2{}^{35}S$ (Amersham 1.1 mL/11.2 mg) was dissolved in the solution. A water-cooled condenser was fitted to the flask, and 12.7 mL (107 mmol) of benzyl bromide was added all at once. The mixture was stirred for 30 min and refluxed for 1 h, and the majority of solvent was removed by distillation. The residue was partitioned between a 5% HCl solution and ether. The aqueous layer was extracted twice more with ether, and the combined ethereal solutions were dried over $MgSO_4$. The solvent was removed by distillation. The residue was distilled at aspirator pressure through a 5 in. vigreux column to give two fractions collected at 80–90 and 90–92 °C. The first fraction contained unreacted benzyl bromide and some product. The second fraction, 6.52 g or 49.1%, was pure benzyl mercaptan by ^{1}H NMR. The literature bp is 195 °C at 760 mm. The specific activity was 2.98×10^9 cpm/mol.

Trifluoromethyl Benzyl Sulfide-^{35}S. A Pyrex flask equipped with a stir bar and a dry ice condenser was charged with 6.20 g (49.9 mmol) of benzyl mercaptan-^{35}S. Approximately 200 mL of liquid ammonia was

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distilled into the flask to form a clear solution. A condensed volume, 4.25 mL (d = 2.36) (51.1 mmol), of trifluoromethyl iodide was distilled in through a cannula. The stirred solution was photolyzed by a low-pressure Hg-vapor lamp from a distance of 20 cm for 30 min.[23] After solvent evaporation, the residue was partitioned between 5% NaOH solution and ether. The ether was extracted twice more with small volumes of base solution and dried over anhydrous magnesium sulfate. The solvent was removed by distillation, and the residue was distilled at aspirator pressure through a 5 in. Vigreux column to give a small forerun and 2.39 g or 24.9% yield of a second fraction at 80 °C containing pure sulfide according to ^{1}H NMR. The yield is variable and was for unknown cause almost 3 times higher on a previous cold run with unlabeled starting material. The literature bp is 76–77 °C at 30 mm.[24] ^{1}H NMR ($DCCl_3$) δ 67.26 (s, 5), 4.04 (s, 2). The specific activity was 9.04×10^8 cpm/mol.

Trifluoromethyl Benzyl Sulfone-^{35}S. The procedure was adapted from ref 25 with 2.28 g (11.9 mmol) of sulfide prepared above oxidized by 2.74 g (17.3 mmol) of $KMnO_4$ in glacial acetic acid at ~0 °C. The workup gave 2.31 g or 86.9% yield of white crystals. The mp 103–104 °C was in agreement with the literature value.[24] ^{1}H NMR ($DCCl_3$) δ 7.44 (s, 5), 4.48 (s, 2). The specific activity was 8.98×10^8 cpm/mol.

Potassium (Trifluoromethane)sulfonate-^{35}S. The procedure was adapted from ref 26. A 10-mL flask equipped with a water-cooled condenser and a stirring bar was charged with 2.00 g (8.92 mmol) of trifluoromethyl benzyl sulfone, 2.85 g (18.0 mmol) of potassium permanganate, 0.010 g of potassium carbonate, and 6 mL of water. The mixture was refluxed and vigorously stirred for 18 h; during this period the sulfone was occasionally scraped back down into the reaction flask from the condenser. The mixture was cooled slightly, and 2–3 mL of ethanol was added to destroy excess oxidant.[27] After another 3 h of reflux the mixture was suction filtered hot. The brown solid filter cake was rinsed with several small portions of water. The combined aqueous solution was acidified to approximately pH 2; a voluminous white precipitate formed. The mixture was extracted three times with an equal volume of ether, and the water was removed by evaporation. The white crystalline residue was dried in vacuo. The ^{1}H NMR in D_2O showed no peaks other than residual H_2O. The ^{19}F NMR gave a singlet, −3.06 relative to trifluoroacetic acid in an external capillary, as did an authentic sample of inactive potassium (trifluoromethane)sulfonate. An organic soluble salt free from other inorganic contaminants was prepared below to find the specific activity.

Triphenylmethylphosphonium (Trifluoromethane)sulfonate. A 50% aqueous acetone solution was prepared from 2.00 g (5.60 mmol) of (triphenylmethyl)phosphonium bromide in a minimum of solvent and 1.45 g (5.64 mmol) of silver (trifluoromethane)sulfonate dissolved in a minimum of distilled water were mixed. The yellow precipitate which formed immediately was filtered and washed with additional aqueous acetone. The clear solution was extracted with three volumes of chloroform. The chloroform solution was dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo to give 2.28 g or 95% yield. The salt was recrystallized from chloroform/ether at low temperature: mp 138.5–140 °C; ^{1}H NMR ($DCCl_3$) δ 7.73–7.59 (m, 15), 2.94 (d, J_{PH} = 13.2 Hz, B). Anal.: Calcd for $C_{20}H_{18}F_3O_3PS$: C, 56.34; H, 4.25%. Found: C, 56.02; H, 4.25.

Triphenylmethylphosphonium (Trifluoromethane)sulfonate-^{35}S (2). A 50% aqueous acetone solution of 0.85 g (2.0 mmol) of unlabeled **2** was prepared in a minimum of solvent and was mixed with a concentrated aqueous solution of 0.16 g (0.84 mmol) of potassium (trifluoromethane)sulfonate-^{35}S. This homogeneous soluton was extracted three times with equal volumes of chloroform. The organic layer was dried over magnesium sulfate, filtered, and dried in vacuo to give 0.80 g or 94% recovery of **2**-^{35}S. The ^{1}H NMR and melting point were identical with those of the unlabeled salt. The specific activity was 8.9×10^7 cpm/mol. This procedure removes the inorganic contaminants in the potassium salt described above.

Methyl (Trifluoromethane)sulfonate Identity Kinetics. Reactions were run at 15 and 35 °C with 0.01 M of the labeled salt **2** and 0.4 M methyl (trifluoromethane)sulfonate in a 25 mL total volume of solution of sulfolane/dimethyl sulfone or pure sulfolane, respectively. A 3.0-mL aliquot was taken periodically and extracted twice with 8.0 mL of salt–ice bath chilled ether. The combined cold ethereal solution was extracted twice with 3.0-mL portions of ice-cold distilled water. Then, the clear ethereal solution was treated with 0.30 g of triphenylphosphine. The phosphine readily dissolved, and almost immediately a cloudy precipitate formed of the salt **2**. This entire process was done as quickly as possible, usually in less than 5 min. Later, an oil or white crystals had formed in each sample which was dissolved by addition of 1–2 mL of spectrograde acetone. The solutions were dried over magnesium sulfate and filtered, and the solvent was removed. The crystals or sometimes an oil thus obtained was recrystallized by dissolution in 1–2 mL of chloroform and 2–3 mL of ether and left for ~10 h in a −14 °C freezer. Occasionally, a very small seed crystal of unlabeled salt **2** was added to induce crystallization. This had no observable effect on the specific activities of the isolated salts. The crystals were identical with starting salt by melting point and ^{1}H NMR. The activities ranged from 100 from early points to the theoretical high of 6000 cpm/g. Background radiation was 40 cpm. The activities were calculated by subtracting background counts and dividing by the total weight of salt counted. The activities of the infinity point were directly measured for each run, and a plot of ln (A_{inf} - A_t) vs. t gave pseudo-first-order plots with slope = k_{obsd}. The k_2 was calculated by $k_2 = k_{obsd}/([ester] + [salt])$.

Stopped-Flow Measurements on the Reaction Rates of Iodide Anion with Methyl Triflate and Dimethyl Sulfate. Rates were followed spectrophotometrically at 265 nm near the methyl iodide maximum, using a Durrum 110 stopped-flow spectrophotometer coupled to a Biomation 805 transient recorder. The contents of the transient recorder could be inspected qualitatively on an oscilloscope. The data were transferred to a computer which did an unweighted least-squares analysis. Reactions were run with an excess of methylating agent (0.1–0.2 M for MeOTf, 0.9–1.0 M for Me_2SO_4, and $1–8 \times 10^{-3}$ M for iodide). The second-order rate constants were determined by dividing the pseudo-first-order rate constant from the usual first-order plot by the concentration of the excess methylating agent. Attempts to follow disappearance of I^- spectrophotometrically were totally unsuccessful.

Studies of the Ionization of Methyl Triflate in Sulfolane. With use of a solvent of dimethyl sulfone in sulfolane, 0.01 to 0.4 M solutions of methyl triflate were made. ^{19}F NMR spectra were taken with a capillary of trifluoroacetic acid in D_2O as a reference. Peak heights were recorded. No other peaks were observed. The NMR tubes were suspended in a 35 °C bath. ^{19}F NMR were taken at 10 min, 9 h, and 19 h. Methyl triflate appears δ + 1.30 from reference and triflate anion δ - 2.04.

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Registry No. $MeOSO_3Me$, 77-78-1; MeO_3SCH_3, 66-27-3; MeI, 74-88-4; MeOTf, 333-27-7; 4-$MeOC_6H_4SO_3Me$, 6214-19-3; 4-$CH_3OC_6H_4Se^+Me_2$, 98652-07-4; 4-$CH_3C_6H_4Se^+Me_2$, 98652-08-5; 3-$CH_3C_6H_4Se^+Me_2$, 98652-09-6; $C_6H_5Se^+Me_2$, 45694-91-5; 4-$ClC_6H_4Se^+Me_2$, 45797-97-5; 4-$CNC_6H_4Se^+Me_2$, 98652-10-9; 4-$NO_2C_6H_4Se^+Me_2$, 46112-09-8; 4-ClC_6H_4SeMe, 37773-29-8; C_6H_5SeMe, 4346-64-9; 4-$CH_3C_6H_4SeMe$, 37773-35-6; 3-$CH_3C_6H_4SeMe$, 1528-87-6; 4-$CH_3OC_6H_4SeMe$, 1694-07-1; 4-$NO_2C_6H_4SeMe$, 43022-52-2; 4-CNC_6H_4SeMe, 98652-11-0.

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