organic phase was dried over $Na_2SO_4$, filtered, and concentrated under vacuum to give 1.26 g (80%) of 1,5-DTCN monosulfoxide: mp 67–70 °C; IR (Nujol) 1010 cm$^{-1}$ (S → O); $^1H$ NMR (CDCl$_3$) $\delta$ 3.2 (m, 4, -CH$_2$S), 2.7 (m, 4, -CH$_2$S), 2.0 (m, 6, -CH$_2$-); $^{13}C$ NMR (CDCl$_3$) $\delta$ 47.8, 46.5, 31.8, 29.4, 26.5, 19.3, 17.4; mass spectrum (70 eV) $m/e$ (rel intensity) 162 (53), 161 (21), 120 (31), 88 (60), 87 (93), 55 (100).

Anal. Calcd for $C_7H_{14}OS_2$: C, 47.15; H, 7.91. Found: C, 46.92; H, 7.66.

**2,6-DTHP Monosulfoxide from 2,6-DTHP Dication.** Into a small flask was placed 0.287 g (2.1 mmol) of 2,6-DTHP. The flask was connected to the reaction tube containing 0.738 g (4.2 mmol) of nitrosyl hexafluorophosphate. The apparatus was connected to a vacuum line and degassed. Dry propionitrile (10 mL) was condensed into both the flask of 2,6-DTHP and the tube of nitrosyl hexafluorophosphate. The solutions were allowed to come to room temperature and then cooled to 0 °C in an ice–water bath. The 2,6-DTHP in propionitrile was added slowly (by rotating the flask) to the rapidly stirring solution of nitrosyl hexafluorophosphate in propionitrile. The solution became a red-brown color immediately on mixing and bubbled vigorously as the nitric oxide was evolved. After all the 2,6-DTHP had been added, the solution became pale yellow and then clear and colorless. The evolved nitric oxide was measured and found to be 3.9 mmol (93%). The reaction flask was removed from the vacuum line, and the solution was poured into a saturated aqueous sodium bicarbonate solution. The resulting mixture was extracted three times with chloroform. The combined organic phase was dried over $Na_2SO_4$, filtered, and concentrated under vacuum to give 0.269 g (84%) 2,6-DTHP monosulfoxide. Yields for all of the other monosulfoxides synthesized by this method are in Table II.

### References and Notes

(1) W. K. Musker and T. L. Wolford, *J. Am. Chem. Soc.*, **98**, 3055 (1976).
(2) W. K. Musker and P. B. Roush, *J. Am. Chem. Soc.*, **98**, 6745 (1976).
(3) P. T. Cottrell and C. V. Mann, *J. Electrochem. Soc.*, **116**, 1499 (1969).
(4) B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1748 (1973).
(5) M. Bonifácié, H. Mockel, D. Bahnemann, and K.-D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, 675 (1975).
(6) D. Bahnemann and K.-D. Asmus, *J. Chem. Soc., Chem. Commun.*, 238 (1975).
(7) (a) S. F. Nelsen and P. J. Hintz, *J. Am. Chem. Soc.*, **94**, 7108 (1972); (b) S. F. Nelsen and R. T. Landis, *ibid.*, **96**, 1788 (1974); (c) S. F. Nelsen and P. J. Hintz, *ibid.*, **94**, 3138 (1972); (d) *ibid.*, **92**, 6215 (1970).
(8) S. F. Nelsen and C. R. Kessel, *J. Am. Chem. Soc.*, **99**, 2392 (1977).
(9) R. W. Alder, R. Gill, and N. C. Goode, *J. Chem. Soc., Chem. Commun.*, 973 (1976).
(10) J. R. L. Smith and L. A. V. Mead, *J. Chem. Soc., Perkin Trans. 2*, 1172 (1977).
(11) Shine and co-workers have shown that thianthrene and related aromatic compounds form cation radicals and dications but there are no sulfur–sulfur bonds in these molecules. H. J. Shine and L. Piette, *J. Am. Chem. Soc.*, **84**, 4798 (1962), and subsequent references.
(12) P. B. Roush, Ph.D. Thesis, University of California, Davis, 1977.
(13) R. J. Gillespie, J. Passmore, P. K. Ummat, and O. C. Vaidya, *Inorg. Chem.*, **10**, 1327 (1971).
(14) H. Meerwein, K.-F. Zenner, and R. Gipp, *Justus Liebigs Ann. Chem.*, **688**, 67 (1965).
(15) D. M. Roush and C. H. Heathcock, *J. Am. Chem. Soc.*, **99**, 2337 (1977).
(16) A. Hirschon, personal communication.
(17) S. F. Nelsen and J. M. Buschek, *J. Am. Chem. Soc.*, **95**, 2011 (1973).
(18) N. J. Allinger and J. L. Coke, *J. Am. Chem. Soc.*, **81**, 4080 (1959).
(19) C. G. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, *Inorg. Chem.*, **10**, 2781 (1971).
(20) S. M. Johnson, C. A. Maier, and I. C. Paul, *J. Chem. Soc. B*, 1603 (1970); A. Yethon, Ph.D. Thesis, University of Illinois.
(21) J. T. Doi and W. K. Musker, *J. Am. Chem. Soc.*, in press.
(22) A detailed analysis of the electrochemistry of these dithioethers is in progress and will be published shortly.
(23) R. S. Glass, J. R. Duchek, J. T. Klug, and G. S. Wilson, *J. Am. Chem. Soc.*, **99**, 7349 (1977).
(24) C. A. Stein and H. Taube, *J. Am. Chem. Soc.*, **100**, 1635 (1978).
(25) W. K. Musker, B. V. Gorewit, P. B. Roush, and T. L. Wolford, *J. Org. Chem.*, in press.
(26) R. H. Eastman and G. Kritchevsky, *J. Org. Chem.*, **24**, 1428 (1959).
(27) A. J. Speziale, "Organic Syntheses". Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 401.
(28) N. B. Tucker and E. E. Reid, *J. Am. Chem. Soc.*, **55**, 775 (1933).
(29) J. R. Meadow and E. E. Reid, *J. Am. Chem. Soc.*, **56**, 2177 (1934).
(30) N. J. Leonard, T. W. Milligan, and T. L. Brown, *J. Am. Chem. Soc.*, **84**, 4075 (1962).
(31) L. A. Ochrymowycz, C.-P. Mak, and J. D. Michna, *J. Org. Chem.*, **39**, 2079 (1974).
(32) M. Protina, J. O. Jilek, and O. Exner, *Chem. Listy*, **47**, 580 (1953); *Chem. Abstr.*, **49**, 155d (1953).
(33) D. Jerchel, L. Dippelhofer, and D. Renner, *Chem. Ber.*, **87**, 947 (1954).

# Reactivity in Methyl Transfer Reactions.[1] 2. Leaving Group Effect on Rates with Substituted Thiophenoxides

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**Abstract:** Rates are reported for the reaction of various methylating agents ($CH_3X$) with the *p*-nitrophenoxide ion and several substituted thiophenoxides in sulfolane solution. The leaving groups, X, in increasing order of rate with thiophenoxide ion are $O_3SCH_3$, *p*-$O_3SC_6H_4CH_3$, $O_3SOCH_3$, I, $O_3SF$, $O_3SCF_3$, $^+O(CH_3)_2$. The rates vary from $10^2$ to more than $10^8$ M$^{-1}$ s$^{-1}$ in this series. With substituted thiophenoxides methyl tosylate and methyl iodide show identical substituent effects, but methyl trifluoromethanesulfonate is slightly but significantly less sensitive to substituents. Trimethyloxonium ion is even less selective, but the rate is approaching the diffusion limitation. The preparatively useful reaction of methyl triflate with phenoxide ion in ethanol solution emphasizes the persistence of considerable selectivity even with very reactive reagents.

Organic chemists have learned to expect very reactive reagents to be rather indiscriminate, and this expectation is now virtually an article of faith. The concept, dating from the early considerations of Polanyi,[2] has been variously restated and updated from qualitative, quantitative, empirical, and theoretical aspects.[3] Nevertheless, the concept has been questioned and counterexamples have been found, for example the work of Ritchie[4] and the extensive review of Johnson.[5]

The reactivities of arylated nucleophiles toward methylating agents $CH_3X$ might be described by the Hammett equation, the Swain–Scott equation,[6] or even the Ritchie equation,[4] although these nucleophiles are not generally listed with ap-

**Table I.** Methylation of *p*-Nitrophenoxide Ion in Sulfolane at 42 °C

| leaving group X of CH$_3$X | $k,^a$ M$^{-1}$ s$^{-1}$ |
|---|---|
| O$_3$SCF$_3$ | 3100$^{b,c}$ |
| O$_3$SF | 1100 |
| O$_3$SOCH$_3$ | 0.85$^c$ |
| I | 0.105$^d$ |
| *p*-O$_3$SC$_6$H$_4$CH$_3$ | 0.0196$^c$ |

$^a$ Concentrations of potassium *p*-nitrophenoxide were within a factor of 2 of 5 × 10$^{-5}$ M. $^b$ The number reported previously, 1300, was a typographic error. $^c$ From ref 1. $^d$ This was believed before to be too slow to measure, when it was anticipated that it would be slower than the tosylate.

propriate *n* or $N^+$ values, but the applicability of the Hammett equation in this limited series implies the Swain–Scott treatment with *s* corresponding to the Hammett $\rho$ and *n* related to the Hammett $\sigma$. Furthermore, the equivalent Swain–Scott and Hammett forms could become entirely equivalent to the Ritchie formulation if the $\rho$ (or *s*) were constant and independent of the leaving group X.

In the first paper of this series,[1] relative reactivities for the nucleophiles *p*-nitrophenoxide ion and phenoxide ion were measured by a competitive method showing that the relative reactivities (or values of $\rho$) were clearly not constant, although the variation among different leaving groups was small. Quantitatively, the competitive method used suffered for two reasons. First, there was a major effect of concentration and nature of the counterion, which was plausibly related to ion-pairing effects. Extrapolation to reasonably dilute solution was unreliable because the method lost precision in solutions less than a few hundredths molar. The second problem was that sulfolane is far from inert to bases,[7] and the rate of protonation of sodium phenoxide by this reaction was significant, especially when the less reactive leaving groups were being studied.

Here we minimize both of these problems and also get more useful data by direct spectrophotometric determination of the reaction rates, which allows the use of concentrations of the order of 5 × 10$^{-5}$ M with the nucleophiles used, and using substituted thiophenoxides rather than phenoxides, the basicity is reduced to a point where the reaction with sulfolane does not seriously interfere. However, the reaction with the more basic nucleophiles with substituents of low $\sigma$ still requires precautions and with the less reactive methylating agents a perceptible correction on the rates. In spite of these problems, we continue to use sulfolane, because of its very low nucleophilic character, high dielectric constant (44 at about 30 °C), UV transparency (useful down to 200 nm when freshly purified), and very low toxicity.[8] We have not measured temperature dependencies of the rates, because of thermostating problems in the stopped flow, and because of the 28 °C melting point of the solvent.

The results of rate measurements on the methylation of potassium *p*-nitrophenoxide in sulfolane are given in Table I which expands (and corrects) the measurements in the first paper.[1] The faster reaction rates are here measured by stopped-flow methods. The rate of reaction of trimethyloxonium fluoroborate, previously reported as too fast to measure, has not been measured, although it is doubtless well within the range of the stopped-flow method. No measurements on the unsubstituted phenoxide were attempted because of the instability of the solutions.

Results of measurements on various substituted thiophenoxides are presented in Table II. The accuracy of most of these values is believed to be within about 5%, although reproducibility was often better. The smallest numbers have the largest errors from the solvent reaction and also from the photolysis of the *p*-nitrothiophenoxide, described in the Experimental Section, so the uncertainties may be larger. The

value for unsubstituted thiophenoxide with the trimethyloxonium tetrafluoroborate is virtually at the upper limit of measurability with a solvent of this viscosity under our conditions, its precision certainly not better than ±10%. This rate is also very close to the diffusion-controlled limit calculated for the viscosity of the solvent (8 cP at 40 °C);[8] direct measurement of this limit awaits a reagent of higher extinction coefficient. The last column shows the relative rates of the *p*-nitro and unsubstituted compounds expressed logarithmically. It is proportional to the Hammett $\rho$, but very rough since there are only two points and the appropriate substituent constant ($\sigma$ or $\sigma^-$) is not clear.

The selectivity, given by log ($k_H/k_{NO_2}$), is seen to be perceptibly lower for the last three entries, which also represent the fastest reactions. This loss of selectivity is clearly not due to the onset of diffusion control (except in the last case where this is a real possibility) and therefore can be attributed to a more reagent-like transition state.

The change of sensitivity is also demonstrated in the three cases in which all five substituents were studied. Hammett plots are poor, because the rate retardation by the *p*-CF$_3$ group is in every case greater than that for the *p*-NO$_2$ group. If the $\sigma^-$ constants are used and the *p*-CF$_3$ group is omitted, the fit is adequate and the values of $\rho = -1.8, -1.8$, and $-1.6$ for X = *p*-toluenesulfonate (OTos), iodide, and trifluoromethanesulfonate (OTf), respectively. Still more convincing, because a choice of substituent constants is unnecessary,[9] and because all five substituents are included, are the plots of Figure 1, in which the rates with one leaving group are plotted logarithmically against those for another. The slope of the plot of rates with CH$_3$I vs. those with CH$_3$OTos is 0.99, with a standard deviation of 0.022, but the plot of CH$_3$OTf vs. CH$_3$OTos rates gives a slope of 0.90 with a standard deviation of 0.055. This is essentially the same as the ratio of $\rho$ values (1.64/1.80 = 0.91) and is probably less than unity, although not with 90% confidence. The conclusion that the triflate rates are less sensitive to substituent than the tosylates, which react about 20 000 times slower, is in accord with a more reagent-like transition state for the former. However, methyl iodide reacts 173 times more rapidly than methyl tosylate, yet is essentially equally selective. Possibly the reduction in selectivity occurs only when the rates get very large but there are not yet enough data to be sure. It is of some interest in connection with solvent effects on substituent constants to note that the fit of the points for *p*-CF$_3$ is good here.

The results are related to those of Berg, Metzger, and coworkers,[10] who found that plotting the logarithm of relative rates with methyl fluorosulfonate against those with methyl iodide gave a good line of the much smaller slope 0.69 for a series of perceptibly hindered pyridine nucleophiles. For experimental reasons the two methylating agents were studied in different solvents, and unfortunately substituent effects are often solvent sensitive,[11] so this more striking effect may not be more significant.[12]

As in the previous work, the effect of leaving groups on the selectivity as the reactivity changes by more than four powers of ten is perceptible. Nevertheless, the error by assuming a $\rho$ independent of the leaving group (as in the Ritchie equation) is remarkably small.

Another aspect of nucleophile-leaving group influences is illustrated in Figure 2. This logarithmic plot of rate constants for attack by *p*-nitrophenoxide vs. those for attack by *p*-nitrothiophenoxide by the various CH$_3$X is nicely linear for the various sulfonates, with a slope of 1.16 and a good fit ($r = 0.9996$) over a range of more than 10$^4$ in rate, but methyl iodide fits badly.

The slope of 1.16 in Figure 2, showing a somewhat greater range of reactivity of the slower reacting oxygen nucleophile than that of the sulfur nucleophile, might be considered a more

**Table II.** Rates for the Reactions of $CH_3X$ with $YC_6H_4S^-$ in Sulfolane at 42 °C

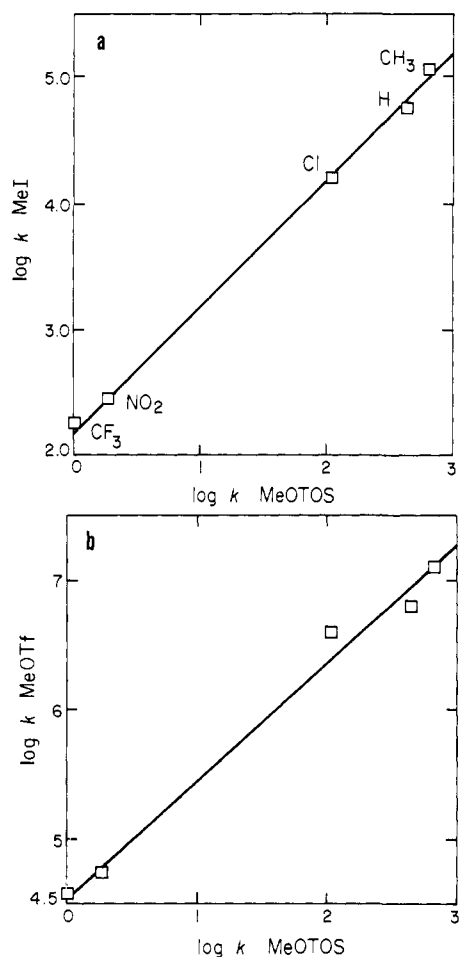| leaving group X | para substituent | | | | | $\log(k_H/k_{NO_2})$ |
|---|---|---|---|---|---|---|
| | $CH_3$ | H | Cl | $CF_3$ | $NO_2$ | |
| $O_3SCH_3$ | | 104 | | | 0.62 | 2.23 |
| $p$-$O_3SC_6H_5CH_3$ | 659 | 434 | 106 | 1.0 | 1.86 | 2.37 |
| $O_3SOCH_3$ | | $1.01 \times 10^4$ | | | 36.9 | 2.44 |
| I | $1.14 \times 10^5$ | $5.67 \times 10^4$ | $1.59 \times 10^4$ | 173 | 279 | 2.31 |
| $O_3SF$ | | $2.79 \times 10^6$ | | | $2.88 \times 10^4$ | 1.99 |
| $O_3SCF_3$ | $1.25 \times 10^7$ | $6.35 \times 10^6$ | $3.87 \times 10^6$ | $3.88 \times 10^4$ | $5.47 \times 10^4$ | 2.06 |
| $O^+(CH_3)_2$ | | $1.9 \times 10^8$ | | | $4.09 \times 10^6$ | 1.66 |



**Figure 1.** (a) Logarithmic plot of rates of reactions of substituted thiophenoxides with methyl iodide vs. those with methyl $p$-toluenesulfonate. The individual para substituents are shown, and the slope is 0.99. (b) The same plot except that the rates with methyl trifluoromethanesulfonate are plotted vertically. The slope is 0.90.



**Figure 2.** Logarithmic plot of rates of reaction of $p$-nitrophenoxide ion ($k_0$) with various methylating agents vs. the rates of $p$-nitrothiophenoxide ($k_s$). The leaving groups are identified, and the slope of the line drawn through the sulfonates is 1.16. Methyl iodide deviates conspicuously.

striking example of loss of selectivity with reactivity, since the loss is accompanied by only about a 17- to a 15-fold increase in reactivity. However, the experimentally less certain competitive rate ratios of the phenoxide to $p$-nitrophenoxide[1] are smaller than those with the thiols. Thus factors determining selectivity beyond only reactivity appear to operate.

The pronounced deviation of methyl iodide in the plot of Figure 2 is in the direction of the "soft–soft" interaction between leaving group and attacking group as described by Pearson and Songstad.[13] An equivalent but more conspicuous manifestation is the observation that methyl iodide is less reactive than dimethyl sulfate with the oxygen nucleophile, but more reactive with the sulfur nucleophiles.

The rather small change in selectivity as the leaving group changes is carried over to very large differences in the nucleophile in an observation of preparative significance. Methyl
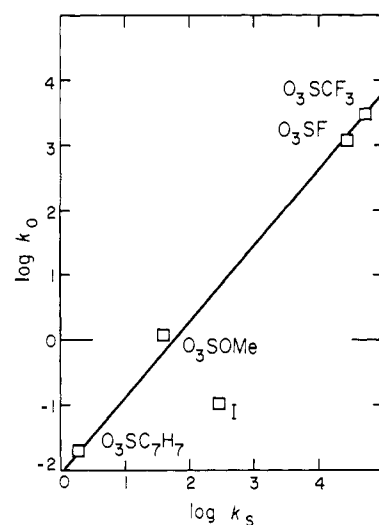
triflate reacts with ethanol very rapidly on a preparative time scale, and ethanol appears to be an unsuitable solvent for methylations with this reagent. Nevertheless, when 1 M solution of sodium phenoxide in ethanol was treated with a 27% excess of methyl triflate, with a good stirring, anisole was produced in 97 ± 5% yield (by gas chromatography). Anisole is also an important product from methyl triflate and aqueous sodium phenoxide, although the yield was not measured. The reaction with ethanol or water, although fast, is clearly not competitive with the reaction with the much better nucleophile phenoxide ion. This selectivity for nucleophiles in aqueous or ethanolic solutions is reminiscent of Peterson's reactions of cyclic halonium salts with aqueous nucleophiles.[14] Apparently, even his very reactive electrophiles react with water at much less than the diffusion-controlled rate. Bromide ion and methanol with the three-membered cyclic bromonium ions compete more evenly, but bromide is still favored.[15] Nevertheless, the rates of some nucleophilic substitution reactions are now seen to be near the diffusion-controlled limit, and the most reactive leaving groups have not yet been thoroughly studied.

## Experimental Section

**Materials.** Tetrahydrothiophene 1,1-dioxide (sulfolane) was purified as described before.[1] When purified in this way, it is an entirely satisfactory UV solvent, but general absorption in the UV develops with time, so that material purified within 1 week was always used.

The various potassium thiophenoxides were prepared by adding aqueous carbonate-free potassium hydroxide to a solution of about 1% excess substituted thiophenol in ethanol, evaporating to dryness under vacuum, and drying the resulting mixture to constant weight in a Fischer pistol. The salts were analyzed for potassium gravimetrically as the tetraphenylboride. The properties were (with UV data in sulfolane solution) as follows. Potassium thiophenoxide (Anal.

Calcd for $C_6H_5SK$: K, 26.4. Found: K, 26.4) $\lambda_{max}$ 308 nm, $\epsilon$ 16 200. Potassium *p*-nitrothiophenoxide (Anal. Calcd for $C_6H_4NO_2SK$: K, 20.2. Found: 20.1) $\lambda_{max}$ 505 nm, $\epsilon$ 25 000. Potassium *p*-chlorothiophenoxide (Anal. Calcd for $C_6H_4ClSK$: K, 21.4. Found: K 20.8) $\lambda_{max}$ 320 nm, $\epsilon$ 17 300. Potassium *p*-methylthiophenoxide (Anal. Calcd for $C_7H_7SK$: K, 24.1. Found: K, 23.9) $\lambda_{max}$ 320 nm, $\epsilon$ 17 200. Potassium *p*-trifluoromethylthiophenoxide (Anal. Calcd for $C_7H_4F_3SK$: K, 18.1. Found: K, 17.8) $\lambda_{max}$ 331 nm, $\epsilon$ 16 000.

*p*-Trifluoromethylthiophenol was prepared from *p*-trifluoromethylaniline (Aldrich) following the method of Tarbell and Fukushima[16] for related compounds. It was obtained in one attempt only in 10% yield, bp 65 °C (20 Torr).

Potassium *p*-nitrophenoxide was prepared as before.[1]

The methylating agents should be handled with caution in a good hood. They have long been known to be toxic, methyl trifluoromethanesulfonate is labeled "cancer suspect," and inhalation of methyl fluorosulfonate has been fatal.[17] For the present purpose it is also necessary that the extent of contamination with acid be very low.

Methyl methanesulfonate was distilled from calcium hydride, bp 38 °C (1 Torr). Dimethyl sulfate was distilled from calcium hydride, bp 35 °C (1 Torr). Methyl *p*-toluenesulfonate was washed with water, dried over anhydrous magnesium sulfate, then distilled from calcium hydride, bp 125 °C (1 Torr). Methyl iodide was washed successively with aqueous sodium bisulfite, water, dilute sodium carbonate, and water, then dried over calcium chloride and distilled (bp 44 °C) from calcium hydride. Methyl fluorosulfonate was distilled from calcium hydride, bp 94 °C. Methyl trifluoromethanesulfonate was distilled from calcium hydride, bp 99 °C. Trimethyloxonium tetrafluoroborate was recrystallized from nitrobenzene and liquid sulfur dioxide.[18] The commercial material was unsuitable without this purification.

**Rate Measurements.** Rates were followed spectrophotometrically at the thiophenoxide 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, and quantitative outputs were taken on a potentiometric recorder. Most runs were made with an excess of methylating agent, but some were checked with excess thiophenoxide; the result was the same within a percent. The rate constants were calculated by dividing the pseudo-first-order rate constant, obtained from the usual first-order plot, by the average concentration of the excess reagent.

Runs with potassium *p*-nitrothiophenoxide were complicated by its photolability, even sometimes in the spectrophotometer. Such runs were therefore done in a room illuminated only by an innocuous red light, and the spectrophotometer slit was reduced to about 0.1 mm. Under these conditions solutions were adequately stable.

The position of methylation was checked by the same method used before on phenoxide ion. Curiously, the methylation with methyl iodide in an aqueous ethanol medium did produce about 2% paramethylated thiophenol, but none was detected in the sulfolane medium. A similar solvent effect on ambient alkylation has been observed previously.[19]

**Methylation in Ethanol.** A 1 M solution of sodium phenoxide in ethanol was placed in a flask and stirred vigorously with a magnetic stirrer. Methyl triflate in 27% excess was added dropwise at room temperature. An internal standard for gas chromatography was added and the mixture was partitioned between ether and water; the ether extracts were concentrated and put on the gas chromatograph. The yield of anisole based on phenoxide calculated by this method was 97 ± 5%.

A similar qualitative experiment in water without the internal standard again showed a significant yield of anisole.

### References and Notes

(1) Part 1 of this series is not so numbered: E. S. Lewis and S. H. Vanderpool, *J. Am. Chem. Soc.*, **99**, 1946 (1977).
(2) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).
(3) J. E. Leffler, *Science*, **117**, 340 (1953); G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955); M. H. Mok and J. C. Polanyi, *J. Chem. Phys.*, **51**, 1451 (1969); L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 35 (1963); and many others.
(4) C. D. Ritchie and P. O. I. Virtanen, *J. Am. Chem. Soc.*, **94**, 4666 (1972).
(5) C. D. Johnson, *Chem. Rev.*, **75**, 755 (1975).
(6) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).
(7) A. Schriesheim, T. J. Wallace, and J. E. Hofmann, *J. Am. Chem. Soc.*, **85**, 2739 (1963).
(8) Technical Bulletin 524, Phillips Petroleum Co.
(9) For examples, see H. L. Pfluger, *J. Am. Chem. Soc.*, **60**, 1513 (1938), as applied to the Brønsted catalysis law; ref 5; D. S. Kemp and M. L. Casey, *J. Am. Chem. Soc.*, **95**, 6670 (1973); ref. 11.
(10) U. Berg, R. Gallo, J. Metzger, and M. Chanon, *J. Am. Chem. Soc.*, **98**, 1260 (1976).
(11) Examples showing variation of $\rho$ in both directions with change in solvent dielectric are given: R. Fuchs and E. S. Lewis in "Technique of Chemistry", Vol. 6, Part 1, E. S. Lewis, Ed., Wiley-Interscience, New York, N.Y., 1974, Chapter 14.
(12) In a prepublication private communication, Professor E. Arnett has shown us some data on pyridine methylation rates indicating a behavior more like Ritchie's than those of ref 10.
(13) R. G. Pearson and J. Songstad, *J. Org. Chem.*, **32**, 2899 (1967).
(14) P. E. Peterson, B. Stevens, S. Magaha, and P. M. Henricks, unpublished manuscript kindly sent to us by Professor Peterson.
(15) P. D. Bartlett and D. S. Tarbell, *J. Am. Chem. Soc.*, **58**, 466 (1936).
(16) D. S. Tarbell and D. K. Fukushima, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 809, and references cited therein.
(17) D. M. W. Van den Ham and D. Van Der Meer, *Chem. Br.*, **12**, 362 (1976).
(18) J. K. Stille and J. A. Empen, *J. Polym. Sci., Part A-1*, **5**, 273 (1967).
(19) N. Kornblum, P. J. Berrigan, and W. J. LeNoble, *J. Am. Chem. Soc.*, **85**, 1141 (1963).