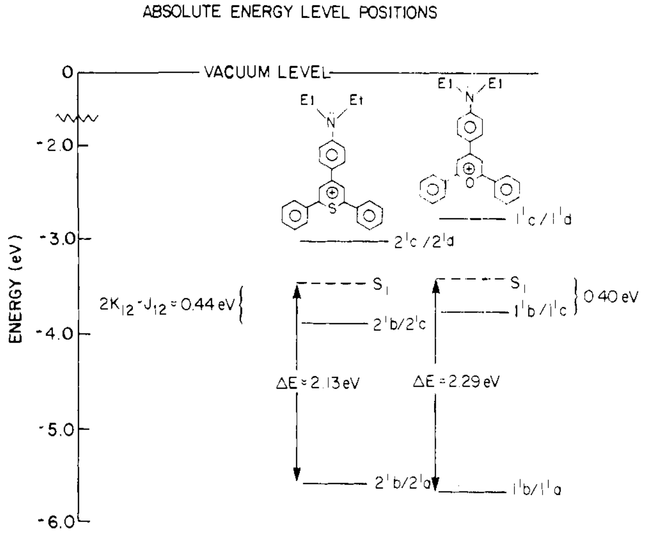

Figure 5. Absolute position of singlet and electrochemical redox levels for 4-(4'-diethylaminophenyl)-2,6-diphenylpyrylium fluoroborate (**1'b**) and 4-(4'-diethylaminophenyl)-2,6-diphenylthiapyrylium fluoroborate (**2'b**) in CH_3CN.

moiety is more electron withdrawing than pyrylium. The wavelength of the intramolecular charge transfer electronic transition in thiapyrylium (**2'b**), i.e., red shifted from pyrylium (**1'b**), also supports this conclusion.

Conclusion

Measurement of the redox levels for two series of pyrylium and thiapyrylium salts has provided a quantitative comparison of the effect of oxygen vs. sulfur on the thermodynamic stabilities to electron transfer of nitrogen-cationic, carbon-radical, and carbon-anionic centers in a single system. The ionic and radical species localized on the pyrylium-thiapyrylium ring system prefer to be adjacent to sulfur. The order of greatest sulfur preference in the 4-(4'-diethylaminophenyl)-2,6-diphenylpyrylium (thiapyrylium) system is the following: anion > radical and radical > cation for the HOMO and LUMO levels, respectively. The wavelength of the intramolecular charge-transfer band and the electrochemical reduction potentials indicate that the thiapyrylium moiety is more electron withdrawing than pyrylium. Sulfur was found to produce a somewhat larger separation between the energy of the first excited singlet (E_{S_1}) and the energy of the lowest unoccupied molecular orbital (E_{LUMO}), obtained electrochemically, than oxygen in the thiapyrylium-pyrylium system studied.

Acknowledgment. We would like to thank G. A. Page for samples of **1'b** and **2'b** and D. J. Sandman for many stimulating discussions.

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Reactivity in Methyl Transfer Reactions. 4. Powerful Methylating Agents with Neutral Nucleophiles

Edward S. Lewis,* Semyon Kukes,[1a] and Carl D. Slater[1b]

Contribution from the Department of Chemistry, Rice University,
P.O. Box 1892, Houston, Texas 77001. *Received April 13, 1979*

Abstract: Rates and activation energies for methyl transfer to a series of substituted phenyl methyl sulfides from methyl trifluoromethanesulfonate (triflate) and from trimethyloxonium tetrafluoroborate are reported, along with rates for reaction of a few substituted dimethylanilines and pyridine with methyl triflate and dimethyl sulfate. The rate constants (in sulfolane) are not very high; varying from about 70 for pyridine and methyl triflate to 9.6×10^{-5} M^{-1} s^{-1} for dimethyl sulfate with *N,N*-dimethyl-*m*-nitroaniline (at 30 °C) and do not provide consistent support for a loss of selectivity with increasing reactivity. With the uncharged phenyl methyl sulfide, trimethyloxonium ion is less than three times more reactive than methyl triflate, in contrast to the factor of 75 reported earlier for the *p*-nitrothiophenoxide ion. The substantial values of the Hammett ρ, the fairly large activation energies, and the persistence of considerable selectivity all suggest that these reactions do not have highly reagent-like transition states. The similarities of rates and activation energies for the reaction of the sulfides with the charged trimethyloxonium ion and the neutral methyl triflate, however, suggest that product solvation is not far along at the transition state.

In previous papers[2-4] methyl transfer rates have been studied with respect to the influence of the leaving group X on the relative reactivities of several nucleophiles Nu_i^- in reaction 1.

$$\mathrm{Nu}_i^- + \mathrm{MeX} \xrightarrow{k+} \mathrm{Nu}_i\mathrm{Me} + \mathrm{X}^- \qquad (1)$$

Not surprisingly, the reactions (with $\mathrm{Nu}_i^- = \mathrm{Ar}_i\mathrm{O}^-$ and $\mathrm{Ar}_i\mathrm{S}^-$) fitted the Hammett equation for variation in Ar_i within normal error limits. One aim was to look for a trend toward loss of selectivity (ρ closer to zero) for the most reactive methylating agents. Small effects in this direction were observed, but it was unclear that the differences in ρ were anything other than random fluctuations, except in the extreme case where there was a possible diffusional limitation.

An unselective, early transition state, case should be char-

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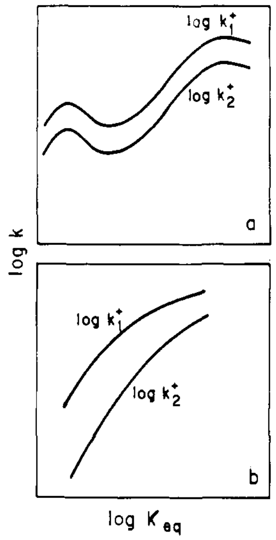

Figure 1. Possible nonlinear log k_1^+ and log k_2^+ vs. log K_{eq} plots which would give linear log k_1^+ vs. log k_2^+ plots. (a) An unlikely plot which would give a linear log k_1^+ vs. log k_2^+ plot of unit slope. (b) A more plausible plot which would give a linear log k_1 vs. log k_2 plot of less than unit slope.

Table I. Rate Constants (in M^{-1} s^{-1} of Methylation of Substituted Phenyl Methyl Sulfides

substituent in $XC_6H_4SCH_3$	MeOTf[a]	MeOTf[b]	$Me_3^+OBF_4^-$[c]
p-CH_3O			8.2×10^{-1}
p-CH_3	1.9×10^{-1}	3.2×10^{-3}	6.0×10^{-1}
H	1.2×10^{-1}	1.2×10^{-3}	3.5×10^{-1}
p-Cl	6.8×10^{-2}	4.5×10^{-4}	1.8×10^{-1}
m-Cl	4.8×10^{-2}	1.7×10^{-4}	1.4×10^{-1}
3,4-Cl_2[d]	3.0×10^{-2}	6.5×10^{-5}	

[a] In sulfolane containing 5.25 mol % dimethylsulfone at 30 °C by stopped flow. The order of one in methyl triflate was determined by initial concentration variation by about a factor of 4. [b] In $CDCl_3$ by NMR at 34 °C. [c] In sulfolane containing 5.25 mol % dimethylsulfone at 30 °C by stopped flow. The order in the oxonium ion was assumed to be one. [d] 3,4-Dichlorophenyl methyl sulfide.

acterized by a small value of ρ^+, the Hammett ρ for the forward reaction (or other measure of selectivity), to be compared with ρ^+ for a reaction with a late, product-like transition state best with ρ_{eq} for the equilibrium constant for the reaction. Implicit in this treatment is that, with each leaving group X, the Hammett equation is obeyed for both the forward rate constants k^+ and the equilibrium constants K_{eq}. If this is the case, then a plot of log k^+ vs. log K_{eq} will also be linear with the slope ρ^+/ρ_{eq}. Such a plot has special advantages: it does not require a decision on the particular σ scale (for example σ, σ^-, or σ°) and can be expected to work for a much wider range of substituent changes than the Hammett series.

If two different leaving groups X_1 and X_2 both have log k_1^+ and log k_2^+ correlating with σ, than a plot of log k_1^+ vs. k_2^+ will also be linear (with a slope ρ_1^+/ρ_2^+). When applied to the Brønsted equation, this is the test applied by Pfluger,[5] and by Johnson[6] to test selectivity variation. This test has been applied,[2] giving linear plots, and lending credence to the assumption of universal applicability of LFE relationships. Nevertheless, although the linear log k_1^+ vs. log k_2^+ plots are a rigorous consequence of two linear log k^+ vs. log K_{eq} plots, the reverse is not necessarily true. Figure 1a shows a sketch of absurdly nonlinear plots of log k^+ vs. log K_{eq}, which would nevertheless lead to a linear log k_1^+ vs. log k_2^+ plot with unit slope, and Figure 1b shows two much more plausible rate-equilibrium plots, which could give a linear log k_1^+ vs. log k_2^+ (in this case with a slope less than unity). These counterexamples show the importance of getting both rate and equilibium data, even if major deviations from LFE relations are not anticipated.[7]

Table II. Activation Energies for Methylation of Substituted Phenyl Methyl Sulfides in Sulfolane[a]

substituent X in $XC_6H_4SCH_3$	E_a, kcal/mol	
	MeOTF[b]	Me_3O^+[c]
p-OCH_3		13.3
p-CH_3	12.4	13.1
H	12.1	12.3
p-Cl	12.8	12.7
m-Cl	12.7	12.2
3,4-Cl_2	12.1	

[a] Containing 5.25 mol % dimethylsulfone to lower the melting point. [b] The differences are probably not significant; the average value is 12.4 ± 0.3 kcal/mol. [c] Not significantly different; the average is 12.7 ± 0.5 kcal/mol.

One study did indeed establish equilibrium data as well as rate data (for the case $Nu_i^- = Ar_iS^-$, $X^- = PhS^-$)[4] and confirmed over a small range the linearity of a log k^+ vs. log K_{eq} plot. In this nearly symmetrical reaction, as expected, $\rho^+ \approx 0.5\rho_{eq}$. Unfortunately, the high temperatures and the use of the solvent ethanol prevented direct correlation with the other available data. In a study of alkylation of substituted pyridines, Arnett and Reich[8] have shown relations between rate constants and overall enthalpy changes, although equilibrium data are not reported in this short communication.

The study reported in this paper lays the kinetic ground work for later work in which we shall report thermodynamics and substituent effects on equilibria for some of these methylations of uncharged nucleophiles. It also attacks the question of the magnitude of electrostatic interactions by comparing trimethyloxonium ion with the neutral methylating agents.

Results and Discussion

The rates of reaction of several substituted phenyl methyl sulfides in sulfolane (tetrahydrothiophene 1,1-dioxide) with methyl triflate (trifluoromethanesulfonate) and with trimethyloxonium tetrafluoroborate were measured at 30, 40, and 50 °C by the stopped-flow method, by using excess methylating agent to achieve pseudo-first-order conditions. Rates of reactions of methyl triflate with the substituted phenyl methyl sulfides in chloroform-*d* were measured by the change in the NMR spectrum. The results at 30 °C are shown in Table I, and the activation energies calculated from experiments also at 40 and 50 °C are given in Table II. No substituent effect on the activation energies appears outside of experimental error; nor are the two methylating agents distinguishable either.

The rates fit the Hammett equation adequately, giving for methyl triflate in sulfolane (at 30 °C) $\rho = -1.06$, in $CDCl_3$ at 34 °C, $\rho = -2.2$ (a normal solvent effect on ρ) and for trimethyloxonium fluoroborate at (30 °C) $\rho = -1.24$. The values of ρ in sulfolane did not show any temperature dependence, within experimental uncertainty. The value for the more reactive trimethyloxonium ion is clearly not less than the value for the methyl triflate in the same solvent; thus, no significant selectively-reactivity correlation is found. The difference in the other direction may not be significant. These values of ρ^+ are about half the value that can be crudely estimated in ρ_{eq}.[9]

Interestingly, the rate for trimethyloxonium ion is only about three times that for methyl triflate, which corresponds to about the same rate per methyl group. In contrast, with *p*-nitrothiophenoxide anion, the oxonium salt is about 75 times as reactive as methyl triflate.[3] Presumably the extra factor of 25

Table III. Rates of Reaction of Some Amines with Methyl Triflate and Dimethyl Sulfate

amine	methyl triflate[a] k, $M^{-1}\,s^{-1}$	dimethyl sulfate[b] k, $\times 10^5$, $M^{-1}\,s^{-1}$
p-$Me_2NC_6H_4NMe_2$	c	5850
$C_6H_5NMe_2$	20.5	207
m-$NO_2C_6H_4NMe_2$	0.35	9.6
pyridine[d]	73.4	1680

[a] Measured by stopped flow in sulfolane at 30 °C. [b] Measured spectrophotometrically in sulfolane at 30 °C. [c] No reproducible results were obtained with this combination; one problem, although not apparently the major one, is the slow production of the radical cation (Wurster's blue) from the diamine, as shown by the ESR spectrum. [d] The absorbance of pyridine at 258 nm increases with methylation.

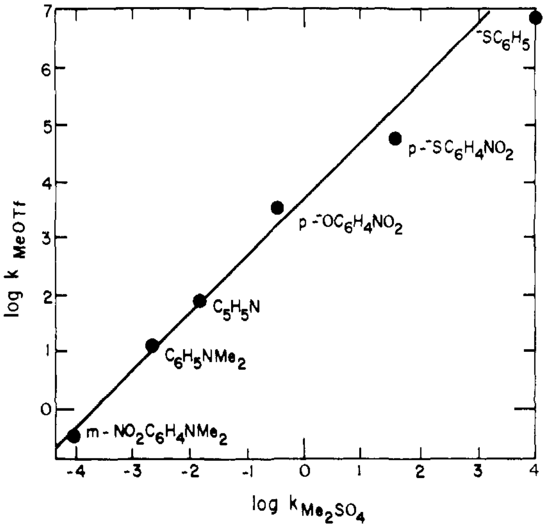

Figure 2. Relative reactivities of methyl triflate and dimethyl sulfate with various nucleophiles. The line drawn of unit slope corresponds to a constant relative reactivity of 4500.

is attributable to the favorable cation-anion interaction with the charged nucleophile. The similarities of rate and activation energy suggest that there is no gross difference in the solvation change on activation, even though the methyl triflate reaction produces ions from neutral molecules. The solvent orientation about these ions may occur later in the course of the reaction.

In another comparison by Kevill and Lin[10] of trimethyloxonium ion and methyl triflate, at about 0 °C in acetonitrile, the former was faster by a factor of about 5, and at −23 °C in methanol the oxonium salt was again faster, by a factor of about 12. They also compared the reactivity in acetonitrile at −23 °C with the weak anionic nucleophile benzenesulfonate. Here the oxonium ion was about 13 times as fast as the triflate. We therefore confirm their conclusion that the difference in reactivity is not very large.

Table III shows reaction rates of some amines with methyl triflate and with dimethyl sulfate, measured by ordinary spectrophotometric and by stopped-flow methods. The precision is not as good as that in Table I because the fast protonation of the amines by acid contaminating methyl triflate solutions is not spectrophotometrically distinguishable from the slower methylation. Thus experiments with a 100-fold excess of methyl triflate would be completely spoiled if 1% of the methyl triflate were converted to triflic acid by adventitious water or other protic substances. The methods used to minimize this problem are described in the Experimental Section.

There are too few data to allow an expression of the substituent effect as a Hammett ρ, except possibly to note that ρ is a substantial negative number. We do not regard the apparently greater effect of the m-nitro group with methyl triflate than with dimethyl sulfate as being highly significant because the result is not confirmed by other substituents. Figure 2 compares the reactivity of methyl triflate and dimethyl sulfate in a log-log plot, and the line of unit slope corresponds to a constant ratio of reactivity of 4500. The deviation for the fastest cases is significant, in the direction again of a reactivity-selectivity fall-off, only a small fraction of which can be attributed to the higher temperature of measurement of the three anionic nucleophiles. Another expression of the deviation is that, toward thiophenoxide, methyl triflate is only 630 times as reactive as dimethyl sulfate, compared with the factor of 4500 which comes close to describing the relative reactivities with all the amines. A related effect was observed before where the slow phenoxide nucleophiles covered a slightly greater range of reactivities with methylating agents than did the faster thiophenoxide nucleophiles.[3]

The slightly greater reactivity of pyridine than dimethylaniline toward methyl triflate is also observed in pyridine solution, where dimethylaniline is perceptibly methylated in the presence of pyridine solvent. However, this kinetic product distribution is not the thermodynamic distribution. When trimethylanilinium triflate is dissolved in pyridine, a slow reaction takes place giving ultimately dimethylaniline and N-methylpyridinium triflate as the only products detectable by NMR. As followed by NMR, at 80 °C this transfer takes place with a rate constant of $5.4 \times 10^{-6}\,M^{-1}\,s^{-1}$, and further studies at 101 and 120 °C gave the activation energy 26.4 kcal/mol. This reaction in pyridine at fairly high temperatures cannot be compared with the other results, but the absence of detectable trimethylanilinium ion at equilibrium shows that the overall free energy change in this methyl transfer is substantially larger than the difference in activation free energies. This result is not very surprising, except possibly that in water solvents the proton transfer equilibrium constant for reaction 2 is very nearly unity.

$$PhNMe_2H^+ + Py \rightleftarrows PhNMe_2 + PyH^+ \qquad (2)$$

Thus there is no close analogy between the proton transfer equilibrium constant in water and the methyl transfer equilibrium constant in sulfolane. We conclude that these neutral nucleophiles are less reactive than the phenoxides and thiophenoxides measured before, and the difference is greater with the cationic trimethyloxonium in them with the neutral methylating agents. We conclude also that there is no compelling evidence here of a drop in selectivity with increasing reactivity; although there are clear differences, they seem to be randomly distributed. Thus combining all the data of this and the earlier papers does not give any compelling evidence either for or against the general operation of the reactivity-selectivity principle in these methyl transfers. The applicability[11] or lack of it[6] of this principle has been extensively discussed, and the effect on this principle of variation in entropies of activation and hence temperature dependence[12] is especially relevant in some cases where it does not apply. There are in fact both examples and counterexamples in the work presented here and in earlier papers.

Experimental Section

Reagents. Aryl methyl sulfides were synthesized by reaction of the corresponding thiophenoxides with methyl iodide. Distillation of the products gave substances with boiling points agreeing closely with values recorded in the literature. The amines employed were commercial (Aldrich Chemical Co.) samples of greater than 98% purity. Dimethylaniline was purifed by distillation from calcium hydride. Pyridine was purified by a literature method.[13] Methyl triflate and dimethylsulfate were distilled from calcium hydride just prior to use.

Trimethyloxonium tetrafluoroborate was a commercial sample purchased from Cationics, Inc. Sulfolane was purified extensively as described previously.[3] Because purified sulfolane has a relatively inconvenient melting point, 30°C, 5.25 mol % dimethyl sulfone was added to lower the melting point and enhance the ease of handling of this solvent. The rare constant for the reaction of *p*-chlorophenyl methyl sulfide with methyl triflate was found to be independent of the presence of this amount of additive, within experimental error.

Kinetic Procedures. Methylation of aryl methyl sulfide was followed by the stopped-flow technique by using a Durrum 110 spectrophotometer. The absorption maximum of each substance in sulfolane was recorded by means of a Cary 14 or Cary 17 spectrophotometer. In all cases, methylation resulted in a large decrease in absorption at 258 nm. Concentrations employed were $\sim 1 \times 10^{-4}$ M for the sulfides, 0.8–0.2 M for methyl triflate, and 0.2 M for trimethyloxonium tetrafluoroborate.

The reactions of pyridine and dimethylanilines were also studied at 258 nm, at which wavelength methylation produced a decrease in absorption with the dimethylanilines and an increase with pyridine. Reactions with dimethyl sulfate were conveniently followed under pseudo-first-order conditions (excess dimethyl sulfate) by using a Cary 14 spectrophotometer with its cell compartment thermostated at 30 °C. With methyl triflate solutions, acidic contaminants in the reaction mixtures probably derived from the reaction of adventitious water with methyl triflate precluded the use of large excesses of methylating agents because the protonated form of the amines simulated spectroscopically the methylated form. These runs were therefore made using second-order conditions with concentrations in the range of 1×10^{-5} to 5×10^{-5} M for dimethylanilines and $\sim 1 \times 10^{-4}$ for pyridine.

Kinetic runs employing NMR measurements were done by using a Varian EM-390 spectrometer. Runs with trimethylanilinium ion in pyridine were conducted in tubes that were sealed under vacuum. The chemical shifts of the methyl group protons were: methyl triflate δ 4.17; phenyl methyl sulfide, 2.43; aryldimethylsulfonium salts, 3.24–3.36; pyridinium ion, 4.43; trimethylanilinium ion, 3.77; and dimethylaniline, 2.75.

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(1) (a) Robert A. Welch Foundation Postdoctoral Fellow. (b) Permanent address: Department of Chemistry, Memphis State Univeristy, Memphis, Tenn.

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Chemiluminescence of Dimethyldioxetanone. Unimolecular Generation of Excited Singlet and Triplet Acetone. Chemically Initiated Electron-Exchange Luminescence, the Primary Light Generating Reaction[1]

Steven P. Schmidt[2a] and Gary B. Schuster*[2b]

Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801.

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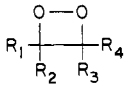
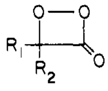
Abstract: Dimethyldioxetanone (**2a**) undergoes two distinct thermal reactions which generate electronically excited states. The unimolecular decomposition of **2a** at 30.0 °C produces excited singlet and triplet acetone, with efficiencies of 0.1 and 1.5%, respectively. The composite activation energy for formation of singlet acetone is 3–4 kcal mol^{-1} greater than the activation energy for the thermal disappearance of **2a**. This result is interpreted in terms of two parallel competitive pathways for dioxetanone decomposition, the more highly activated one of which leads to excited acetone. The addition of easily oxidized aromatic hydrocarbons or amines catalyzes the chemiluminescence of **2a**. The magnitude of the catalytic rate constant and the efficiency of light production are correlated with the one electron oxidation potential of the hydrocarbon. Under these conditions, the chemiluminescence results from a chemically initiated electron-exchange luminescence path.

Considerable insight into the mechanisms of chemiluminescence has been provided by the extensive investigation over the past decade of the chemistry of 1,2-dioxetanes (1).[3] To date nearly 100 of these molecules have been prepared and their properties scrutinized in order to elucidate the mechanistic details of their remarkable transformation to excited state carbonyl-containing products. Meanwhile, only a few of the closely related dioxetanones (2) have been reported.[4] Their study has been hindered by difficulties in synthetic entries[5] and by their thermal and catalytic lability.



1

a, $R_1-R_4 = CH_3$



2

a, $R_1, R_2 = CH_3$

The chemiluminescence of dioxetanones is of particular interest due to their postulated intermediacy in several bioluminescent reactions,[6] including that of the firefly.[7] Prior to their isolation, simple alkyl substituted dioxetanes such as **1a**

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