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Relative Reactivities of Phenoxides with Methylating Agents

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Abstract: The relative reactivities of substituted phenoxide ions toward a range of methylating agents are determined competitively from the yields of substituted anisoles, as well as by direct rate measurement, and show that the selectivity between different phenoxides increases for CH_3X in the order $(CH_3)_3O^+$ (2.8), $CH_3OSO_2CF_3$ (3.5), $CH_3(OSO_3CH_3)$ (5.0), $CH_3O\text{-}P^+CH_3(OCH_3)_2$ (9.5), CH_3OTs (9.6), CH_3I (28). The parenthetical numbers are relative rates of sodium phenoxide and sodium *p*-nitrophenoxide measured competitively in sulfolane solution at total sodium ion concentration of about 0.3 M. The relative rates increase with dilution, by substitution of potassium salts for sodium salts, and by addition of crown ethers, but the difference between methyl trifluoromethanesulfonate and methyl iodide remains substantial. Accuracy is limited by the instability of sodium or potassium phenoxide solutions in sulfolane, but the observed differences in selectivities cannot be attributed to this error. Some absolute rates in other solvents are presented.

Characterization of nucleophilic reactivity has been of interest for many years in a variety of systems. Reasonably successful attempts have been made to correlate rates of nucleophilic substitution on carbon with one another,[1] with basicity alone,[2] or combined with polarizability,[3,4] as well as by calculation.[5] Nucleophilic character has also been assigned by Ritchie[6] on the basis of rates of combination with electrophiles, such as carbonium ions. The current study is concerned with the reaction,

$$Y^- + RX \rightarrow YR + X^- \qquad (1)$$

with the further limitation that the only concern is with the clearly one-step or S_N2 reactions, thus avoiding many of the problems associated with intermediate carbonium ions. Although it has been suggested[7] that ion pairs are intermediate even in S_N2 reactions, there is little question that there is for classical S_N2 examples, a single rate-determining step with a negatively charged transition state containing Y, R, and X in a linear array. Thus the possible existence of a lower energy potential minimum for an R^+X^- ion pair before this transition state is reached is fortunately without relevance to the problem of rate or transition state structure or energy, and this possible complication can be safely ignored. By limiting the structure of R to methyl the S_N2 mechanism is assured and steric interactions are made nearly constant. Furthermore, the methyl is the smallest organic group. Thus substitution on methyl, or "methyl transfer", is a close analogue to the proton transfer reaction, which has been so extensively studied in both rate and equilibrium.[8]

The further rationale for studying reactions of CH_3X is that since much of the early work on nucleophilic reactivity of various compounds RX, a number of very reactive reagents, such as $(CH_3)_3O^+$ and $CH_3OSO_2CF_3$ ("methyl triflate", CH_3OTf) have become available. It appeared of interest to compare these reactive ones with the more conventional methylating agents; perhaps the high reactivity is associated with a low selectivity among different nucleophiles.

Methods and Results

The majority of the experimental work consists in the measurement of relative rates of the reactions

$$MeX + C_6H_5O^- \xrightarrow{k_H} C_6H_5OMe + X^- \qquad (2)$$

$$MeX + p\text{-}O_2NC_6H_4O^- \xrightarrow{k_{NO_2}} p\text{-}NO_2C_6H_4OMe + X^- \qquad (3)$$

by allowing a mixture of the two phenoxides to compete for an insufficiency of MeX, and then determining the apparent rate constant ratio, denoted as $R_{NO_2}{}^H$, from the relative yields of anisole and *p*-nitroanisole, as measured gas chromatographically, using the equation

$$R_{NO_2}{}^H = \frac{(p\text{-}NO_2C_6H_4O^-)_0\, A_{PhOMe} S_H}{(C_6H_5O^-)_0\, A_{p\text{-}NO_2C_6H_4OMe} S_{NO_2}} \qquad (4)$$

in which the concentrations are initial concentrations, the A's are integrated areas of the GC peaks of anisoles, and the S's are the relative GC molar sensitivities with the detector used. This equation actually represents the ratio of the bimolecular rate constants, k_H/k_{NO_2}, for reactions 2 and 3 only if certain assumptions are made: (1) The GC analysis actually gives the correct ratio of the two anisoles in the reaction mixture. This assumption is by no means automatically true, but problems such as the instability, especially of *p*-nitroanisole, on the GC system, fractionation of the anisoles during concentration, and interference of the solvent sulfolane with the analysis were successfully overcome, as shown by control experiments. (2) The relative concentrations of the two phenoxides do not change during the reaction. By choosing initial concentrations

Table I. Relative Reactivities of Sodium Phenoxide and *p*-Nitrophenoxide with CH_3X in Sulfolane at 40 °C

CH_3X	$R_{NO_2}{}^{H\,a}$	Second-order rate constant, k_{NO_2}, 42 °C
$CH_3O^+(CH_3)_2{}^b$	2.8^b	>5000
$CH_3OSO_2CF_3$	3.5	1300
$CH_3OSO_2OCH_3$	5.0	0.85
$CH_3OP^+Me(OMe)_2{}^c$	9.5	
CH_3OSO_2-*p*-$C_6H_4CH_3$	9.6	0.0196
CH_3I	28	

[a] Calculated from eq 4. [b] The reaction rate is very fast; the mixing may be inadequate. [c] Reference 13.

Table II. Effect of Concentration and Nature of Cation in Relative Reactivity[a,b]

MeX	M^+	Concn[c]	$R_{NO_2}{}^H$
MeOTf	Na	0.35	3.5 (6.6)
MeOTf	Na	0.075	7.5 (11.8)
MeOTf	Na	0.01	8.8
MeOTf	K	0.1	16.8 (17.4)
MeI	Na	0.3	28
MeI	Na	0.07	38 (49)

[a] At ~40 °C. [b] Parenthetical numbers are from experiments with about 0.85 equiv of dibenzo-18-crown-6 crown ether. [c] Approximate total salt concentrations.

of phenoxides at least ten times that of MeX, the error from this source becomes insignificant. A further problem of instability of the solutions is mentioned below. (3) The solution is homogeneous throughout the course of the reaction. The problem here is that if the reaction is very rapid, it may occur faster than the mixing rate, and local depletions of phenoxides not helped by the large excess may cause eq 4 to fail, and give an erroneously low selectivity. Absolute rate measurement combined with a method of mixing faster than 1 s, showed that this error was not serious except possibly in one case. (4) The products and reagents are stable to the reaction conditions. All the methylating agents were unaltered in a reasonable length of time in sulfolane solution, sodium and potassium *p*-nitrophenoxide were also stable, but the more strongly basic phenoxide solutions are not stable under these conditions,[9] and this factor is the prime limitation on the accuracy of the results. It will be shown that this error does not alter any of the qualitative conclusions. (5) The anisoles are not produced by any other reaction. The reaction

$$Na^{+-}OC_6H_5 + CH_3X \xrightarrow{k_{H\mathrm{i.p.}}} CH_3OC_6H_5 + Na^+X^- \quad (5)$$

which recognizes both the existence and possible reactivity of ion pairs in this medium, is a possibility of this nature. Because ion pairing is important in this medium and because the ion pairs may themselves be nucleophiles, we use the expression $R_{NO_2}{}^H$ to mean exactly the result of the calculation indicated by eq 4, rather than a demonstrated ratio of rate constants. It should be noted that if the ion pairs are unreactive, then eq 4 adequately describes the rate constant ratios, but these rate constants are influenced by a "salt effect" of considerable magnitude.

A variety of different methylating agents were studied with solutions of sodium phenoxide and *p*-nitrophenoxide and the relative reactivities, $R_{NO_2}{}^H$ are illustrated in Table I. They are not sensitive to the presence of trace acids, for the results are unaltered by the addition of small amounts of potassium *tert*-butoxide. The results usefully order the methylating agents, but do not quantitatively establish the bimolecular rate constants. The total sodium ion concentration is about 0.3 M. These results are relevant to synthetic applications because of the high concentrations.

Table II makes it clear that the apparent relative reactivities are strongly concentration dependent, and that some of the unselectivity of the concentrated solutions is probably related to an ion pairing phenomenon. The first level of explanation is that only the sodium phenoxide is importantly ion paired, and the ion pair is unreactive toward the methylating agents. Thus by tying up the phenoxide ion in an unreactive form, term $(C_6H_5O^-)$ in eq 4 should be reduced from the stoichiometric concentration, and the observed $R_{NO_2}{}^H$ can be expected to be reduced below the true rate constant ratio k_H/k_{NO_2}. If the ion pairing is suppressed by dilution, then k_H/k_{NO_2} should be relatively unaltered, but $R_{NO_2}{}^H$ would approach the rate constant ratio as a limit. This would also carry the prediction that the relative change in $R_{NO_2}{}^H$ with concentration would reflect only the ion-pair equilibrium, and would be insensitive to the nature of X. Thus the rate constant ratio should be

$$k_H/k_{NO_2} = R_{NO_2}{}^H/f_{free}$$

where f_{free} is the fraction of phenoxide in the free or unpaired form. Thus extrapolation to infinite dilution with X = OSO_2CF_3 should allow calculation of f_{free} for all other concentrations, and thus calculation of $R_{NO_2}{}^H$ for various concentrations for X = I. This same calculation should also work with the more reasonable hypothesis that the *p*-nitrophenoxide ion is also subject to ion pairing, presumably to a smaller extent. It is here implicitly assumed that there are no residual salt effects on these reactions of a neutral RX. It is clear that in fact the results with methyl iodide are less sensitive to dilution than those with methyl triflate, suggesting that the ion pair is reactive with at least one reagent. Unfortunately, the values of $R_{NO_2}{}^H$ with methyl iodide are unquestionably low, especially in the more dilute solutions. This is because the phenoxide ion is consumed by its reaction with sulfolane, a reaction which is not fast enough to cause serious problems with the methyl triflate reaction. We thus cannot clearly evaluate the concentration effect on the methyl iodide reactivity.

The effect of changing from sodium ion to potassium ion also is consistent with the ion pairing explanation, as is the effect of adding a crown ether. Apparently the sulfolane-phenoxide reaction rate is also accelerated by these changes, so that the qualitative conclusions are confirmed, and quantitative conclusions are not helped.

We may conclude that for CH_3OTf, $k_H/k_{NO_2} = 20 \pm 3$ and for CH_3I, $k_H/k_{NO_2} > 50$.

The variation of k_H/k_{NO_2} with X is of course expected from the selectivity-reactivity relation; it is incompatible with the Ritchie equation,[6] which would require relative reactivities to be independent of the electrophile and hence independent of X, and Ritchie recognized early that S_N2 reactivities were not closely related to his N_+ values.[6] Nevertheless, the discrepancy is small: if we estimate ρ from the two points only as $\rho = \log(k_H/k_{NO_2})/1.24$, we find $\rho = -1.0$ for X = OTf, and $\rho < -1.4$ for X = I, and the surprising feature is that the highly reactive methyl triflate is as selective as it is.

The absolute reactivities of a few of the methylating agents in sulfolane were estimated by the disappearance of the *p*-nitrophenoxide absorption at 425 nm on mixing the appropriate solutions held at about 42 °C as rapidly as possible in the cell of a Cary spectrophotometer. The rate for CH_3OTf is rough; it was about as fast as could be measured by this method. Methyl iodide was too volatile, and trimethyloxonium ion reacted completely before a recording could be made. The results are presented in Table I.

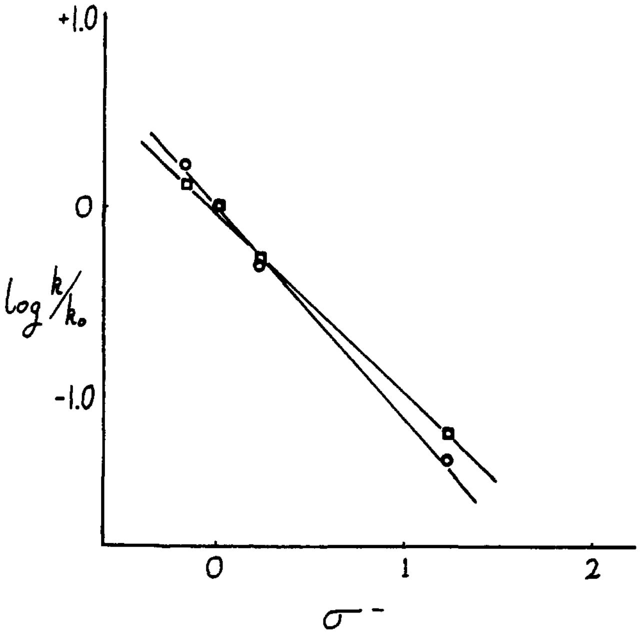

Figure 1. Hammett plots for reaction of methyl iodide (circles), $\rho = -1.1$, and methyl *p*-toluenesulfonate (squares), $\rho = -0.95$.

Bimolecular rate constants for methyl iodide and methyl *p*-toluenesulfonate with several phenoxides were measured in ethanol solution, following the method used for ethyl iodide by Goldsworthy.[10] The rate constant for phenoxide ion at 42 °C was 8.5×10^{-4} L/mol s for the iodide, and 7.3×10^{-3} L/mol s for the tosyl ester. The Hammett plots from these data are shown in Figure 1, which clearly shows a perceptible difference in the values of ρ. The values are for CH_3I, $= -1.1$, and for CH_3OTos, $= -0.93$. The values are lower than in sulfolane, reflecting a common solvent dependence of ρ.[12] These ρ values also conceal the fact that substituted phenoxides are to a significant and substituent dependent extent present in ethanol solutions as neutral phenols. The value of ρ for unsolvolyzed phenoxides would be somewhat more negative.

The high reactivity of methyl triflate (about 1.8×10^5 times that of methyl tosylate) suggests that it might be attacking phenoxide ion (an established ambident ion)[11] at carbon as well as at oxygen. A search for *o*- or *p*-cresol, and their methyl ethers failed to find any amount detectable by gas chromatography, apparently under these conditions C-alkylation is not competitive with O-alkylation.

This work is being continued, with emphasis on the more informative direct rate measurements, and efforts to reduce the extent of nucleophile-solvent reactions.

Experimental Section

Instrumental. Gas chromatographic analysis was performed on a Varian Aerograph Model 550 with a flame ionization detector. The columns used were a ⅛ in. × 12 ft, 10% Apiezon L on Chromosorb P/AW and a ⅛ in. × 12 ft, 20% PMPE + 2% FFAP on Chromosorb P/AW. Peak areas were obtained with an Autolab 6300 digital integrator. Ultraviolet and visible spectra and reaction curves were obtained on a Cary 17 spectrophotometer using 1-cm quartz cells. The reference and sample compartments were heated with a homemade hot air blower for sulfolane solutions, to prevent freezing.

Materials. Absolute ethanol was used without further purification. Tetrahydrothiophene 1,1-dioxide (sulfolane) (Aldrich) was vacuum distilled twice from sodium hydroxide pellets and finally from calcium hydride. The purified sulfolane was stored over calcium hydride in an inert atmosphere.

Trimethyloxonium tetrafluoroborate (Cationics) and iodomethane (Aldrich) were used without further purification. Methyl trimethoxyphosphonium triflate was used as supplied by K. Colle.[13] Methyl trifluoromethanesulfonate (methyl triflate) was freshly distilled before use. Methyl *p*-toluenesulfonate was washed with water, dried, and distilled before use.

Various para-substituted phenoxides were prepared in ethanol solution by the method of Goldsworthy.[10] The sodium and potassium salts of phenol were prepared by adding a 1% excess of freshly distilled phenol to a solution of the corresponding hydroxide. The solvent was distilled off and the wet salt was dried under vacuum to constant weight in a Fisher Pistol at 78 °C using P_2O_5 as the desiccant. Sodium *p*-nitrophenoxide (Eastman), commercially available as the dihydrate, was dried as above. Potassium *p*-nitrophenoxide was prepared by adding excess *p*-nitrophenol to a potassium hydroxide solution and washing with diethyl ether until the ethereal phase did not turn water yellow. The solvent was distilled off and the wet salt was dried as above except at 138 °C.

All salts were at least 99% pure as determined by gravimetric analysis for the metal as sodium or potassium chloride after ashing.

Competitive Rates. In a typical competitive experiment 0.616 g of sodium *p*-nitrophenoxide (3.83×10^{-4} mol) and 0.0235 g of sodium phenoxide (2.03×10^{-4} mol) were dissolved in 7 mL of dry sulfolane and placed on one side of a special reaction flask over calcium hydride. On the other side of the reaction flask was placed 3 mL of dry sulfolane containing 2.5 μL of methyl triflate ($\sim 2.1 \times 10^{-5}$ mol) over calcium hydride. This special reaction flask was made by dividing a round-bottom flask into two chambers by molding a partition into the bottom. Mixing times of <1 s were assured by shaking the reaction flask vigorously. The reaction solution was allowed to react 10–30 min, decanted, and about 100 mL of cold water and 10 mL of cold diethyl ether was added. The ethereal phase was washed three times with 25–50 mL of cold water and dried over anhydrous magnesium sulfate. This procedure gave complete removal of sulfolane, which has a similar retention time to *p*-nitroanisole. The same procedure was used for potassium salts and for cases where crown ether was added. Dibenzo-18-crown-6 was used in these experiments. There is no significance to the choice of only 0.85 equiv of crown ether, but an important effect can be expected.

In a typical direct rate measurement, 2.5 mL of 5×10^{-5} M sodium *p*-nitrophenoxide in sulfolane solution was placed in a 1-cm quartz cell and allowed to equilibrate at 42 °C. A vial of methyl sulfate was also brought to 42 °C and 2.5×10^{-4} mol was added to the cell by syringe to make a 9×10^{-3} M solution. The cell was replaced in the sample compartment and an absorption curve was obtained at 425 nm. Rate constants were calculated from the pseudo-first-order curves obtained.

Search for C-Methylation. To test for possible carbon methylation, methyl triflate was dissolved in dry sulfolane with an excess of sodium phenoxide. After reacting 10 min, water was added and the reaction mixture was extracted with diethyl ether. The ethereal layer was dried over anhydrous magnesium sulfate and gas chromatographic analysis showed only the O-methylation product, anisole. The aqueous layer was allowed to react overnight while stirring with a large excess of iodomethane and extracted with diethyl ether. The ether extract was dried and analyzed by gas chromatography. Analysis showed no methylanisoles as products. *o*- and *p*-methylanisole for GC standards were prepared by the reaction of the corresponding phenolate salt with iodomethane in ethanol.

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Ab Initio SCF Study of the Disrotatory Closure of 1,4-Diaza-1,3-dienes to Diazacyclobutene

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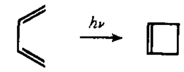
Abstract: An all-electron "ab initio" SCF–CI method is used to calculate the ground and lowest excited states potential energy surfaces for the "linear" reaction path of the disrotatory cyclization of α-diimine to diazacyclobutene. The analysis of these surfaces allows us to rationalize why this reaction, though very similar to the allowed and well-documented closure of butadiene into cyclobutene, is unlikely to occur.

Upon appropriate irradiation, 1,3-dienes may undergo two different electrocyclic reactions.[2] The first reaction, 4π-electron disrotatory closure (eq 1), leads to cyclobutene derivatives;[3] the second reaction, 6π-electron conrotatory opening (eq 2), leads to species characterized by a triene skeleton.[4] Both processes play a prominent role in the Woodward and Hoffmann qualitative analysis of allowed and forbidden electrocyclic reactions.[5] Moreover, the former has lately received quantitative attention.[6,7] 1,4-Diaza-1,3-dienes (α-diimines), though isoelectronic with butadiene, have a somewhat surprising photochemical behavior. These molecules are reluctant to form four-membered 1,2-diazacyclobutene rings by the 4π-electron photoclosure (eq 3).[8] On the other hand, the 6π-electron photovalence isomerization (eq 4) of 1,4-diaza-1,3-dienes into a triene-like structure occurs and has been convincingly documented.[9] This contrasting behavior between dienes and diazadienes could possibly be related to the one basic difference between their respective excited state manifolds: the presence in the latter of low-lying $n\pi^*$ excited states. These states result from the emergence in the diimine system of molecular orbitals of a pair of high-lying occupied n-type wave functions, that is, the familiar in-phase (n_+) and out-of-phase (n_-) combinations of the nitrogen lone pairs. In order to elucidate the rationale behind the "forbidden" character of (3) we have calculated the potential energy surfaces of several low-lying excited states of 1,4-diaza-1,3-dienes for the disrotatory distortion. We shall first briefly outline the profile of these calculations and then proceed to analyze the mechanistic implications of the resulting theoretical curves.



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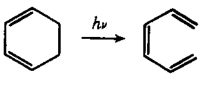

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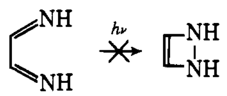

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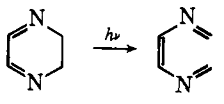

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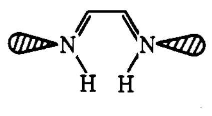
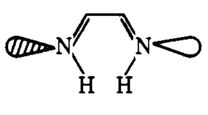


n_+



n_-

Method of Calculation. The disrotatory closure of α-diimine was investigated in a way which closely parallels our study of butadiene itself.[7a] The Gaussian 70 SCF program[10] was used to carry out the Hartree–Fock segment of the calculation. The basis set consists of two parts, that is, the familiar localized STO 3G valence atomic orbitals[11] were complemented by a set of semidiffuse Gaussian p orbitals with optimized exponents of 0.12 (carbon p orbitals) and 0.18 (nitrogen).[12] The three degenerate x, y, and z components were included on each carbon and nitrogen atom. This first SCF step must provide us with MO's which will serve to build the various Slater determinants forming the basis for the configuration interaction (CI) calculation. The best set of MO's must be obtained to ensure that the CI procedure, which for practical reasons, has to be limited, will nevertheless approach as closely as possible the results of a full treatment. In the vicinity of the reactant and product molecules, Roothaan's closed-shell SCF formalism[14] will undoubtedly give us adequate MO's. However, in the intermediate region of the reaction trajectory, where the rising highest occupied MO crosses the stabilized lowest vacant partner, more appropriate MO's are obtained by using Nesbet's brand of open-shell SCF calculation.[15] In fact, we have tried both methods at each point of the reaction path and accepted as final result that which, after completion of the CI, yields the lower energy for the ground state of te system. Finally the CI treatment was carried out in the following manner. The set of MO's whose occupancy is allowed to vary is the union of two smaller groups: (a) the n_+ and n_- pair and the eight π MO's of the diene plus those diene MO's which correlate with π MO's of the cycle and have not yet been counted, and (b) n_+ and n_- of the cycle, which correlate with their diene parents, respectively, the ten π MO's of the cycle plus those cycle orbitals which correlates with π MO's of the diene (prominent among them the σ and σ^* MO's of the newly formed N–N bond). All the one-electron configurations re-