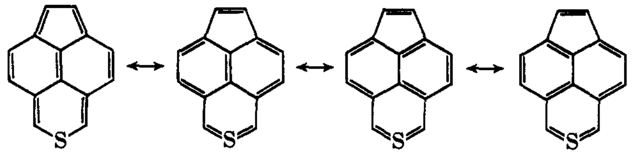
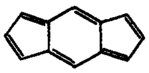


74 **74a** **74b** **74c**

Additional experiments need to be carried out to determine the contribution of tetravalent sulfur resonance structures, since in light of our findings stability of the system alone does not require their inclusion.

Compounds **75–87** are all unknown but represent interesting sulfur heterocycles. While a number appear to be potentially aromatic systems, for example, **82** and **83**, others with negative REPE's should be antiaromatic in their behavior. Of the antiaromatics **75** is particularly interesting. Although it is isoelectronic with *s*-indacene (**88**) (REPE = 0.009β) and similar in



88

structure, it is predicted to be quite antiaromatic (-0.040β).

The above results are further evidence that the Hückel method as presently employed is an extremely useful tool not only in its predictive power but also, and perhaps potentially more important, in gaining a more basic understanding of the nature of aromaticity of cyclic conjugated systems. While earlier treatments of sulfur compounds based on the Hückel method were often helpful,[39] the use of the reference structure as proposed by Dewar greatly increases the reliability of predictions of aromatic character of sulfur heterocycles.

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(39) R. Zahradnik, *Advan. Heterocycl. Chem.*, **5**, 1 (1965).

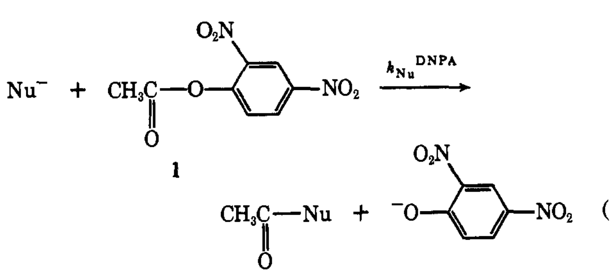
Relative Nucleophilicity of Common Nucleophiles toward Sulfonyl Sulfur. II. Comparison of the Relative Reactivity of Twenty Different Nucleophiles toward Sulfonyl Sulfur *vs.* Carbonyl Carbon[1a,b]

John L. Kice* and Eugenia Legan[1c]

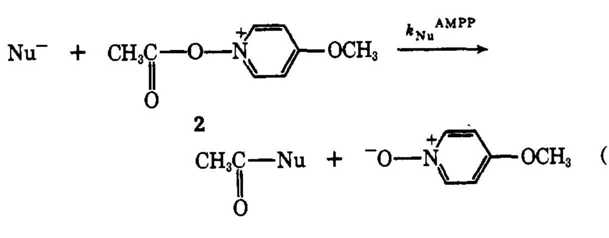
Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05401. *Received January 9, 1973*

Abstract: The rate of reaction of 20 different nucleophiles with phenyl α-disulfone (**3**) at 25° in 60% dioxane has been determined, mainly by stopped-flow techniques. Comparison of the rate constants with those for reaction of the same nucleophiles with 2,4-dinitrophenyl acetate (**1**) or 1-acetoxy-4-methoxypyridinium perchlorate (**2**) reveals that, except for fluoride ion, the relative reactivity of all the nucleophiles toward sulfonyl sulfur can be predicted quite accurately from a knowledge of their relative reactivity toward carbonyl carbon in a substitution involving a leaving group of similar character and p*K*. Since the nucleophiles studied cover a wide range of nucleophile types, this suggests that in general sulfonyl sulfur is very similar to carbonyl carbon as an electrophilic center. The reactivity of HO_2^-, CH_3CONHO^-, and hydrazine indicates that α-effect nucleophiles of all types show enhanced reactivity (an α effect) toward **3** comparable to that which they exhibit in substitutions with **1** and **2**. The reactivity of fluoride ion toward sulfonyl sulfur is greater than would be predicted from its reactivity toward carbonyl carbon by a factor of about 20.

In 1968 Jencks and Gilchrist[2] reported data on the reactivity of about 40 different nucleophiles toward each of a series of four esters, including 2,4-dinitrophenyl acetate (**1**) and 1-acetoxy-4-methoxypyridinium perchlorate (**2**). Because the data for eq 1 and 2 encompass a wide range of types of nucleophiles and were all obtained under a single set of reaction conditions, they offer an unusually comprehensive and reliable storehouse of information on the relative reactivity of nucleophiles in a substitution reaction at a carbonyl carbon bearing a good leaving group (p*K* = 2–4).



(1)



(2)

Kice, Kasperek, and Patterson[1b] have shown that data on the reactivity of nucleophiles in a substitution at sulfonyl sulfur can be obtained by studying reactions of phenyl α-disulfone (**3**) of the type shown in eq 3.

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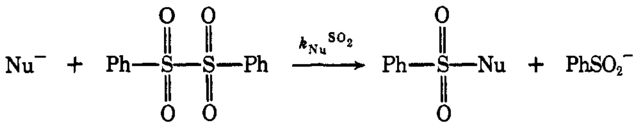
(1) (a) This research supported by the National Science Foundation, Grant No. GP-25799; (b) previous paper: J. L, Kice, G. J. Kasperek, and D. Patterson, *J. Amer. Chem. Soc.*, **91**, 5516 (1969); (c) National Science Foundation Undergraduate Research Participant, summer 1972.

(2) W. P. Jencks and M. Gilchrist, *J. Amer. Chem. Soc.*, **90**, 2622 (1968).

Table I. Kinetics of the Reaction of Selected Anionic Nucleophiles with Phenyl α-Disulfone at 25° in 60% Dioxane[a]

Nucleophile	$10^6(3)$, M	$10^2(Nu^-)$, M	$10^2(NuH)$, M	k_1, sec^{-1} [b]	$k_1/(Nu^-)$, M^{-1} sec^{-1}
CN^-	6.0	2.0	2.0	0.0086	0.43
		1.0	1.0	0.0048	0.48
$CF_3CH_2O^-$	3.0	1.0	9.0	2.3	2.3×10^2
		0.50	9.5	1.2	2.4×10^2
CH_3CONHO^-	3.0	0.50	1.5	4.45	8.9×10^2
		0.30	1.7	2.55	8.5×10^2
HOO^-	3.1	0.50	1.27	27.5	5.5×10^3
		0.20	1.57	10.6	5.3×10^3

[a] All runs with ionic strength of solution held constant at 0.04 by addition of lithium perchlorate. [b] Experimental first-order rate constant for the disappearance of 3.



$$Nu^- + Ph{-}S(O_2){-}S(O_2){-}Ph \xrightarrow{k_{Nu}^{SO_2}} Ph{-}S(O_2){-}Nu + PhSO_2^- \quad (3)$$

3

Benzenesulfinate ion ($PhSO_2^-$), of course, represents a leaving group with a pK roughly comparable[3] to those in **1** and **2**. Comparison of the limited amount of data obtained in this initial study[1b] of nucleophilic substitutions involving **3** with the data[2] for the same nucleophiles reacting with **1** indicated roughly the same pattern of nucleophilic reactivity, but the number of nucleophiles for which the comparison could be made (five) was too small to permit any definitive conclusions to be drawn.

In the present work we have now extended study of the reaction of **3** with nucleophiles to cover a total of 20 of the nucleophiles studied by Jencks and Gilchrist[2] with **1** and **2**, including those "α effect"[5] nucleophiles like HO_2^-, CH_3CONHO^-, and hydrazine that show enhanced reactivity relative to other nucleophiles of comparable proton basicity in many substitution reactions.

The new results make possible an extensive comparison of the relative order of reactivity of nucleophiles toward sulfonyl sulfur *vs.* carbonyl carbon and permit one to draw some fairly definitive conclusions regarding the important similarities and differences in the response of the two centers to changes in nucleophile structure.

Results

Since the previous data[1b] on the reactivity of selected nucleophiles toward **3** were obtained in 60% dioxane as solvent, the same medium was used as the solvent for the present work. The reactions of the various nucleophiles with **3** were all followed under conditions where the nucleophile was present in very large stoichiometric excess over **3**. With the majority of the nucleophiles studied, the rates of disappearance of **3** were sufficiently rapid that the reactions had to be followed by stopped-flow spectrophotometric techniques. With the slower reacting nucleophiles like cyanide ion or imidazole, the rates were slow enough to be followed by conventional ultraviolets pectrophotometry. When possible, reactions were followed at 244 nm, the wavelength where **3** has its absorption maximum. However, when the nucleophile itself absorbed too strongly at this wavelength, appropriate alternate wavelengths in the 258–270-nm region were used. In every event plots of log $(A - A_\infty)$ *vs.* time showed excellent linearity, demonstrating that in each case the disappearance of **3** followed good first-order kinetics.

The nucleophiles investigated fall into two general classes, a group of nitrogen bases of varying structure, and a group of anions. The reactions of the former with **3** were studied in 1:1 buffers of the nitrogen base and its conjugate acid. With the anions, except for cyanide ion, the solutions used contained considerably less of the anion than of its conjugate acid. Almost all of the kinetic data were obtained at a constant ionic strength of 0.04. The results of the various kinetic runs with the anionic nucleophiles are given in Table I, while the results for the runs with the nitrogen bases as nucleophiles are shown in Table II. In each case the rate constant k_1 represents the experimental first-order rate constant for the disappearance of **3** under the reaction conditions in question.

For each reaction where there is a simple first-order dependence on nucleophile concentration, k_1 should be equal to

$$k_1 = k_{Nu}^{SO_2}(\text{nucleophile}) \qquad (4)$$

so that k_1/(nucleophile) should be independent of nucleophile concentration and equal to $k_{Nu}^{SO_2}$, the second-order rate constant for the reaction of that particular nucleophile with **3**. With all of the anionic nucleophiles and with most of the nitrogen ones there is indeed no apparent significant variation in k_1/(nucleophile) with changing nucleophile concentration.

On the other hand, with hydrazine and ethylenediamine k_1/(Nu) does definitely increase somewhat with increasing (Nu). As can be seen from Figure 1, which shows a plot of k_1/(Nu) *vs.* (Nu) for the hydrazine data, the increase is a linear one and is what one would expect if k_1 for these two nucleophiles is given by

$$k_1 = k_{Nu}^{SO_2}(\text{nucleophile}) + k'(\text{nucleophile})^2 \qquad (5)$$

rather than the simpler expression in eq 4.

The simplest mechanistic explanation for the k' term is that it represents general base catalysis by a second molecule of the nucleophile of the attack of a molecule of the nucleophile on **3**. In any event, one can obtain accurate values of $k_{Nu}^{SO_2}$ for hydrazine and ethylenediamine to compare with those for the other nucleophiles by taking the intercept of the plot of k_1/(Nu) *vs.* (Nu) on the k_1/(Nu) axis.

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[3] The reported[4] pK_a of $PhSO_2H$ is 1.2.

[4] C. D, Ritchie, J. D. Saltiel, and E. S. Lewis, *J. Amer. Chem. Soc.*, **83**, 4601 (1961).

[5] J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).

Table II. Kinetics of the Reaction of Various Nitrogen Nucleophiles with Phenyl α-Disulfone at 25° in 60% Dioxane[a]

Nucleophile	10^5(3), M	10^2(Nu), M[b]	10^2(NuH$^+$), M[b]	k_1, sec^{-1} [c]	k_1/(Nu), M^{-1} sec^{-1}
Piperidine	1.55	4.0	4.0	4.9	122
	3.1	4.0	4.0	5.0	125
	1.55	2.0	2.0	2.3	115
	3.1	2.0	2.0	2.4	120
Piperazine	2.7	4.0	4.0	1.95	49
		2.0	2.0	0.93	47
NH_2NH_2	3.0	4.0	4.0	0.95	24
	2.7	3.0	3.0	0.67	22
	3.0	2.0	2.0	0.41	21
	2.7	1.6	1.6	0.30	19
	3.0	1.0	1.0	0.176	17.6
	2.7	0.50	0.50	0.085	17.0
Morpholine	3.0	4.0	4.0	0.49	12.2
		2.0	2.0	0.24	12.0
$H_2NCH_2CH_2NH_2$	2.7	4.0	4.0	0.55	14.2
		2.0	2.0	0.23	11.6
		1.0	1.0	0.104	10.4
NH_2OH[d]	3.1	1.0	1.0	0.0189	1.9
		0.75	0.75	0.0145	1.9
		0.50	0.50	0.0096	1.9
$EtOOCCH_2NH_2$	3.0	4.0	4.0	0.0105	0.26
		2.0	2.0	0.0049[e]	0.24
Imidazole	6.0	4.0	4.0	0.0089	0.22
		2.0	2.0	0.0045	0.22
		1.0	1.0	0.0024	0.24
$H_3^+NCH_2CH_2NH_2$	6.0	2.5	0.50	0.0055	0.22
		1.25	0.25	0.0025	0.20
Piperazine H$^+$	6.0	2.5	0.50	0.0031	0.125
		1.25	0.25	0.00153	0.123

[a] Except where indicated all runs with ionic strength of solution held constant at 0.04 by addition of lithium perchlorate. [b] Solutions prepared by adding calculated amount of standard $HClO_4$ to a solution of the nitrogen base. [c] Experimental first-order rate constant for disappearance of 3. [d] Ionic strength equal to 0.02 in all runs with NH_2OH. [e] Ionic strength = 0.02.

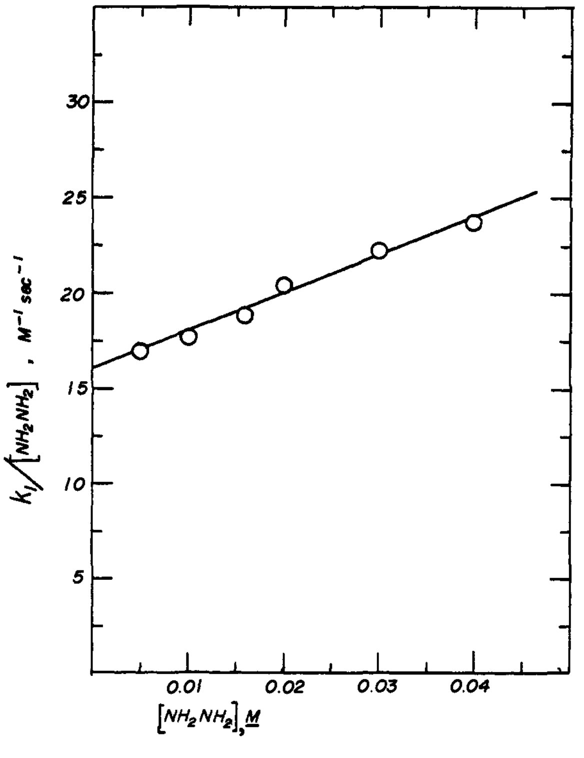

Figure 1. Plot of $k_1/[NH_2NH_2]$ *vs.* $[NH_2NH_2]$ for reaction of hydrazine with 3.

Table III. Summary of Rate Constants for Reactions of Nucleophiles with Phenyl α-Disulfone (3), 2,4-Dinitrophenyl Acetate (1), and 1-Acetoxy-4-methoxypyridinium Perchlorate (2) at 25°[a]

Nucleophile	$k_{Nu}^{SO_2}$,[f] M^{-1} sec^{-1}	k_{Nu}^{DNPA},[g] M^{-1} sec^{-1}	k_{Nu}^{AMPP},[h] M^{-1} sec^{-1}
HOO^-	5.4×10^3	1.62×10^4	2.3×10^6
$CH_3C(O)NHO^-$	870	1.04×10^3	2.2×10^5
$CF_3CH_2O^-$	235	400	4.6×10^4
Piperidine	120	630	6.5×10^3
OH^-	75[b]	54	9.5×10^3
Piperazine	48	420	5.3×10^3
n-$BuNH_2$	17[c]	120[d]	3.4×10^3 [d]
NH_2NH_2	16	300	8.2×10^3
Morpholine	12	80	1.7×10^3
$H_2NCH_2CH_2NH_2$	9.6	110	2.8×10^3
H_2NOH	1.9[e]	47	4.8×10^3
N_3^-	0.94[c]	0.95	380
CN^-	0.45	0.55	73
$EtOOCCH_2NH_2$	0.26	7.8	280
Imidazole	0.23	5.8	820
$H_3^+NCH_2CH_2NH_2$	0.21	5.4	147
F^-	0.18[c]	0.0032	3.7
Piperazine H$^+$	0.124	1.6	60
NO_2^-	0.029[c]	0.0088	8.5
CH_3COO^-	0.0031[c]	0.00057	1.1

[a] Data for **3** are in 60% dioxane as solvent at an ionic strength of 0.04, except as noted. Data for **1** and **2** are in water as solvent at an ionic strength of 1.0 and are from ref 2. [b] Reference 6. [c] Reference 1b. [d] Data are for *n*-propyl- rather than *n*-butylamine. [e] Ionic strength = 0.02. [f] Equation 3. [g] Equation 1. [h] Equation 2.

Discussion

Table III gives the rate constants for the reaction of 20 different representative nucleophiles with phenyl α-disulfone (**3**) in 60% dioxane at 25° (eq 3), either as determined in the present study or measured in earlier work.[1b,6] The last two columns of the table give the rate constants for the reaction of esters **1** and **2**, respec-

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(6) J. L. Kice, *J. Org. Chem.*, 37, 1865 (1972).

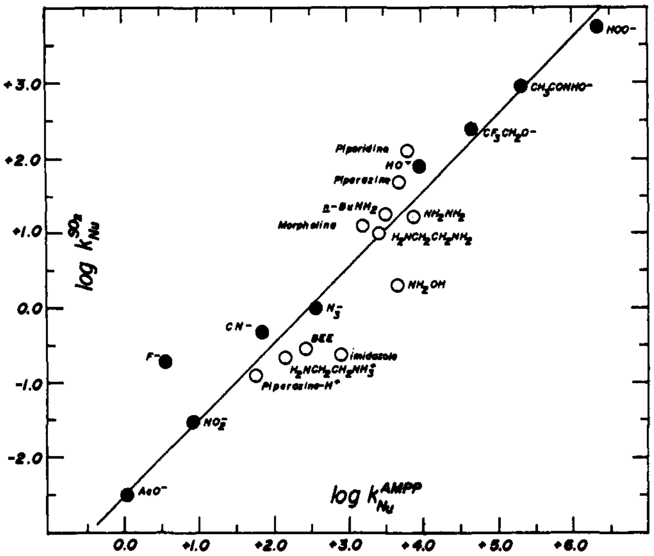


Figure 2. Plot of log $k_{\mathrm{Nu}}{}^{\mathrm{SO_2}}$ for reactions of nucleophiles with **3** *vs.* log $k_{\mathrm{Nu}}{}^{\mathrm{AMPP}}$ for their reactions with **2**. Anionic nucleophiles (●), nitrogen base nucleophiles (○), GEE = glycine ethyl ester. Correlation line drawn with unit slope.

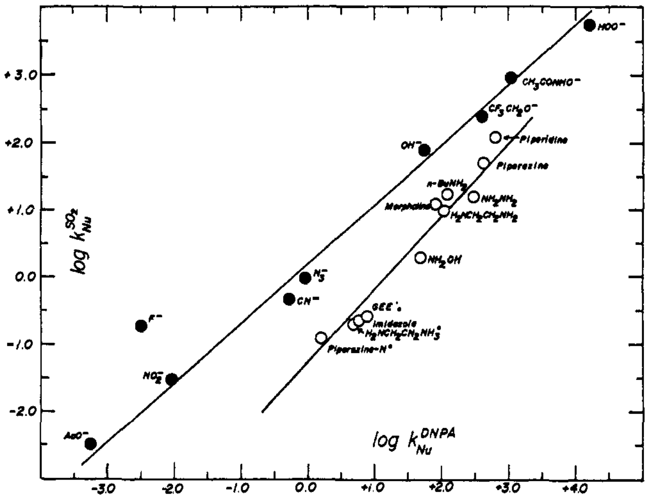


Figure 3. Plot of log $k_{\mathrm{Nu}}{}^{\mathrm{SO_2}}$ for reactions of nucleophiles with **3** *vs.* log $k_{\mathrm{Nu}}{}^{\mathrm{DNPA}}$ for their reactions with **1**. Anionic nucleophiles (●); nitrogen base nucleophiles (○). Correlation line for nitrogen base nucleophiles drawn with slope = 1.1, that for anionic nucleophiles with a slope of 0.90.

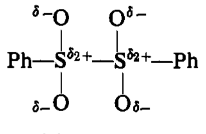
tively, with these same nucleophiles at 25° in pure water as solvent (eq 1 and 2).[2]

Figure 2 shows a plot of log $k_{\mathrm{Nu}}{}^{\mathrm{SO_2}}$ *vs.* log $k_{\mathrm{Nu}}{}^{\mathrm{AMPP}}$ for all of the nucleophiles in Table III. A correlation line of unit slope has been drawn on the plot. Examination of the figure indicates that only three data points (those for fluoride ion, imidazole, and hydroxylamine) deviate really significantly from this correlation line. Fluoride is about 20 times more reactive in the substitution at sulfonyl sulfur than would be expected from its reactivity toward AMPP (**2**); while imidazole and hydroxylamine are both less reactive than expected toward **3** by roughly the same factor. (We will see in a moment, however, that, although fluoride ion also shows markedly exalted reactivity toward the sulfonyl compound when one compares log $k_{\mathrm{Nu}}{}^{\mathrm{SO_2}}$ and log $k_{\mathrm{Nu}}{}^{\mathrm{DNPA}}$, imidazole and NH_2OH do not show any deviation in this latter comparison from the line correlating the behavior of the other neutral nucleophiles. As a result, it is not clear whether any significance should be attached to the deviation of the NH_2OH and imidazole data points in Figure 2.)

Figure 3 shows a plot of log $k_{\mathrm{Nu}}{}^{\mathrm{SO_2}}$ *vs.* log $k_{\mathrm{Nu}}{}^{\mathrm{DNPA}}$ for the nucleophiles of Table III. In this instance the data points cluster on two separate lines, both of approximately unit slope. One line correlates the data for all the nitrogen base nucleophiles; the other, which is displaced from this by about one log unit and has a slightly smaller slope, correlates the data for all the anionic nucleophiles except fluoride ion, F^-, as noted earlier, being markedly more reactive toward the sulfonyl compound than expected based on its reactivity toward DNPA (**1**).

Why are there separate correlation lines for the anionic and nitrogen base nucleophiles when log $k_{\mathrm{Nu}}{}^{\mathrm{SO_2}}$ and log $k_{\mathrm{Nu}}{}^{\mathrm{DNPA}}$ are compared, yet the data for both groups of nucleophiles are correlated by a single line when log $k_{\mathrm{Nu}}{}^{\mathrm{SO_2}}$ and log $k_{\mathrm{Nu}}{}^{\mathrm{AMPP}}$ are compared? In addressing this question it is important first to point out that a plot of log $k_{\mathrm{Nu}}{}^{\mathrm{AMPP}}$ *vs.* log $k_{\mathrm{Nu}}{}^{\mathrm{DNPA}}$ also looks like the one in Figure 3, with the data for the anionic nucleophiles correlated by a separate line from the data points for the nitrogen bases. In the case of these two acetates, this behavior presumably arises because the full positive charge on the leaving group in AMPP causes that substrate to react in general relatively more rapidly with all negatively charged nucleophiles than with those of comparable nucleophilicity not bearing a negative charge. What Figures 2 and 3 therefore seem to indicate is that, even though there is no positive charge on the leaving group in **3**, anionic nucleophiles apparently enjoy a general advantage over neutral nucleophiles in their reaction with **3** in 60% dioxane similar to that which they enjoy in water in reaction with AMPP as compared to DNPA. This is probably simply a reflection of the fact that, because of the lower dielectric constant of 60% dioxane as compared to water, all neutral nucleophiles will be less reactive relative to an anionic nucleophile of comparable nucleophilicity in reaction with an uncharged substrate in this solvent than they are in pure water.

Another possible contributing factor, however, is the following. Although the leaving group in **3** does not bear a formal positive charge, the electronic structure of a sulfonyl group is such that the sulfur atom does bear a substantial partial positive charge; there is therefore in **3** a significant unfavorable inductive interaction between the two adjacent sulfur atoms, *i.e.*



$$\mathrm{Ph{-}}\overset{{}^{\delta-}\mathrm{O}}{\underset{{}_{\delta-}\mathrm{O}}{\mathrm{S}^{\delta_2+}}}\mathrm{{-}}\overset{\mathrm{O}^{\delta-}}{\underset{\mathrm{O}_{\delta-}}{\mathrm{S}^{\delta_2+}}}\mathrm{{-}Ph}$$

Attack of the nucleophile on **3** is presumably the rate-determining step for the reaction of this compound with all of the nucleophiles in Table III.[7] In the case of an

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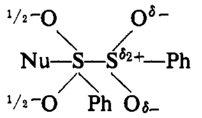
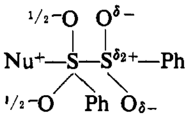
(7) The fact that the pK_a of $PhSO_2H$ is significantly smaller than the pK_a of the conjugate acids of any of the nucleophiles in Table III argues strongly that once any intermediate such as **4a** or **4b** is formed it will break down preferentially by loss of $PhSO_2^-$, so that formation of the intermediate by attack of the nucleophile on 3 should in each case be rate determining. In the event that no actual intermediate was formed, due to bond-making and bond-breaking being synchronous, attack of the nucleophile would, of course, also be rate determining.

anionic nucleophile, formation of a new bond to one sulfonyl group will result in an intermediate (**4a**) in which one of the sulfurs is no longer partially positively charged and the repulsion between the two adjacent sulfurs has been eliminated.[8] On the other hand, with a neutral nucleophilic group, such as the nitrogen bases, the lack of repulsive inductive interaction between the two sulfurs in the intermediate (**4b**) is to a considerable extent offset by the fact that in forming the new bond to sulfur the attacking atom of a neutral nucleophile becomes positively charged and interacts inductively in an unfavorable fashion with the other sulfur. These considerations could cause an anionic nucleophile to enjoy a significant reactivity advantage over a neutral nucleophile of equivalent inherent nucleophilicity toward sulfonyl sulfur and could therefore account for the fact that in its substitution reactions **3** appears to show an effect of this type similar to that found with **2**.[9]



4a



4b

The nucleophiles in Table III cover a considerable range of nucleophile types. They differ widely not only in basicity, but also in polarizability. In hard and soft acid and base theory parlance[10] some, like the oxyanions, are classified as hard bases, while CN^- is considered a soft base, and N_3^- and NO_2^- are thought to be "intermediate" in character. Some of the anions are so-called α-effect nucleophiles, as are also some of the nitrogen bases. Figures 2 and 3 show that, except for fluoride ion, the relative reactivity of all of these nucleophiles toward sulfonyl sulfur can apparently be predicted rather accurately from a knowledge of their relative reactivity toward $>C{=}O$ in a substitution involving a leaving group of comparable character and pK. We conclude from this that in general $>SO_2$ is very similar in character to $>C{=}O$ as an electrophilic center and responds to changes in nucleophile structure in much the same way. Out of the 20 nucleophiles examined, the only significant exception to the last statement would appear to be fluoride ion, which is significantly more reactive toward an $>SO_2$ group than its relative reactivity toward $>C{=}O$ would have led one to expect. It is interesting that in displacements at four-coordinate phosphorus (as in Me(RO)P(O)X), another hard, second-row electrophilic center, fluoride ion shows surprising reactivity compared to its reactivity in substitutions at $>C{=}O$,[11] the effect there apparently being considerably larger than the one observed for the sulfonyl group. Edwards[11] has suggested in the phosphorus case that this may be due to π-bonding involving nonbonded electron pairs on fluorine and unfilled d orbitals on phosphorus.

Let us close with a few comments about what our results indicate regarding the "α effect"[5] in substitutions at sulfonyl sulfur. Two types of α-effect nucleophiles are now recognized.[12,13] One group, of which hydrazine is a representative example, is thought to derive their unusual reactivity from a more favorable $\Delta F°$ for the reaction than would be expected from their basicity toward a proton.[12] While this group of nucleophiles shows markedly enhanced reactivity in substitutions involving carboxylic acid derivatives, stable carbonium ions, etc., they do not do so in SN2 substitutions at the sp^3 carbon of such substrates as methyl iodide or tosylate. The second group of α-effect nucleophiles, of which HO_2^- is a representative example, shows markedly enhanced reactivity toward sp^3 carbon as well as other electrophilic centers and appears to derive a *significant* part of their unusual reactivity from factors *other* than a more favorable $\Delta F°$ for the reaction than predicted from their proton basicity.

By comparing the value of either $k_{HO_2^-}/k_{OH^-}$ or $k_{HO_2^-}/k_{CF_3CH_2O^-}$ for **3** with the rate constant ratios obtained for the reaction of the same pairs of nucleophiles with other appropriate substrates,[12,13] we can get some idea of the relative importance of the α effect for reactions of α-effect nucleophiles of the second type with sulfonyl sulfur as compared with other electrophilic centers. Since glycine ethyl ester (7.9) and hydrazine (8.1) have close to the same pK_a, we can use $k_{NH_2NH_2}/k_{H_2NCH_2COOEt}$ for **3** as compared to $k_{NH_2NH_2}/k_{H_2NCH_2COOEt}$ for other substrates to obtain insight into the relative importance of the α effect for α-effect nucleophiles of the first kind with **3**. Such data are shown in Table IV. In the case of $k_{NH_2NH_2}/k_{H_2NCH_2COOEt}$ the α effect for **3** is somewhat larger than it is for **1** and **2**; in the case of $k_{HO_2^-}/k_{OH^-}$ or $k_{H_2O^-}/k_{CF_3CH_2O^-}$ it is somewhat smaller. The important point to note, however, is that **3**, like the various carboxylic acid derivatives in Table IV, shows a large α effect in substitutions with *both* types of α-effect nucleophiles. This is then a further important respect in which nucleophilic substitutions at $>SO_2$ and $>C{=}O$ appear to show closely similar behavior in terms of their response to changes in nucleophile structure.

Experimental Section

Preparation and Purification of Materials. The preparation and purification of phenyl α-disulfone (**3**) and the method of purifying the dioxane used as solvent have already been described.[1b] Sodium cyanide, lithium perchlorate, hydroxylamine hydrochloride, 30% hydrogen peroxide, and 95% hydrazine were all reagent grade and were used without further purification. Trifluoroethanol, piperidine, morpholine, and ethylenediamine of the highest purity obtainable commercially were fractionally distilled before use. Highest purity commercial samples of imidazole, glycine ethyl ester hydrochloride, and piperazine were recrystallized from appropriate solvents before use. Acetohydroxamic acid was prepared and purified as described in the recent literature.[14]

Procedure for Kinetic Runs. The exact procedure used varied

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[8] The large positive ρ values found[1b,6] for the reaction of anionic nucleophiles with $ArSO_2SO_2Ar$ indicate that there is indeed a large increase in electron density at the reaction site on going from reactants to rate-determining transition state in nucleophilic substitutions involving **3**.

[9] The arguments given here have been developed assuming that the substitutions with **3** involve an actual intermediate (**4**) on the reaction coordinate. However, the same conclusions would also be reached if one were to assume that bond-making and bond-breaking were synchronous and that no actual intermediate was ever formed. This is so because it is the strong unfavorable inductive interaction of the two sulfurs in **3** itself, rather than any specifics about the timing of covalency changes in the actual substitution, which is the origin of the effect.

[10] R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967).

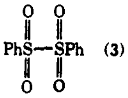
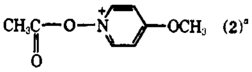
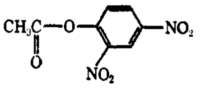
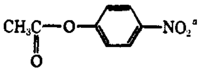
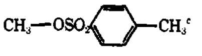
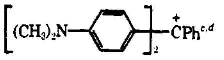
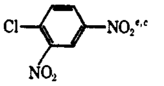
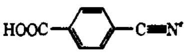
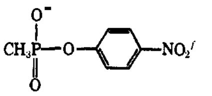
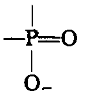
[11] J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1964, pp 59-60.

[12] J. E. Dixon and T. C, Bruice, *J. Amer. Chem. Soc.*, **93**, 6592 (1971); **94**, 2052 (1972).

[13] J. E. McIsaac, L. R. Subbaraman, J. Subbaraman, H. A. Mulhausen, and E. J. Behrman, *J. Org. Chem.*, 37, 1037 (1972).

[14] J. W. Munson and K. A. Connors, *J. Amer. Chem. Soc.*, **94**, 1980 (1972).

Table IV. α Effects for Different Nucleophiles with Various Substrates

Substrate	Electrophilic center	$k_{HO_2^-}/k_{OH^-}$	$k_{HO_2^-}/k_{CF_3CH_2O^-}$	$k_{NH_2NH_2}/k_{H_2NCH_2COOEt}$
 (3)	>SO$_2$	72	24	60
 (2)[a]	>C=O	240	50	30
 (1)[a]	>C=O	300	40	38
 [a]	>C=O	77	58	44[b]
 [c]	sp^3 carbon	45	57	0.9[b]
 [c,d]	$\geqslant C^+$	10^4		28[b]
 [e,c]	sp^2 carbon	300		35[b]
 [e]	—C≡N	1000		
p-Nitrophenyl sulfate[f,c]	>SO$_2$	125		6.0[b]
 [f]	 $-\overset{\vert}{\underset{\underset{O^-}{\vert}}{P}}=O$	50		

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[a] Reference 2. [b] Data are for $k_{NH_2NH_2}/k_{glycylglycine}$ or $k_{NH_2NH_2}/k_{H_2NCH_2CONH_2}$ rather than for $k_{NH_2NH_2}/k_{H_2NCH_2COOEt}$. [c] Reference 12. [d] J. E. Dixon and T. C. Bruice, *J. Amer. Chem. Soc.*, **93**, 3248 (1971). [e] Reference 13. [f] E. J. Behrman, M. J. Biallas, H. J. Brass, J. O. Edwards, and M. Isaks, *J. Org. Chem.*, **35**, 3069 (1970).

depending on whether the reaction was to be followed by stopped-flow or by conventional ultraviolet spectrophotometry and upon whether the purified form of the nucleophile was the nucleophile itself or its conjugate acid.

In those cases (hydroxylamine hydrochloride, glycine ethyl ester hydrochloride, hydrogen peroxide, trifluoroethanol, and acetohydroxamic acid) in which the purified form of the nucleophile was the conjugate acid, solutions of the nucleophile of the proper concentration were prepared by adding a calculated amount of standard sodium hydroxide solution in 60% dioxane (v/v) to a known amount of the conjugate acid of the nucleophile in the same solvent. The proper amount of standard lithium perchlorate solution, if any, needed to bring the final ionic strength to the desired value was then added and the solution was made up to volume. In those cases (cyanide, piperidine, piperazine, hydrazine, morpholine, ethylenediamine, and imidazole) in which the purified form of the nucleophile was the nucleophile itself, a buffer solution of the nucleophile and its conjugate acid of the desired concentration was prepared by adding a known amount of standard perchloric acid solution to a known amount of the nucleophile in 60% dioxane. Here too, if needed, the ionic strength was adjusted to the desired value by the addition of standard lithium perchlorate solution.

For the runs followed by stopped-flow procedures, stock solutions of **3** were prepared by dissolving a carefully weighed amount of the α-disulfone in 25 ml of dioxane. This solution (2 ml) and 1.3 ml of water were pipetted into a 50-ml volumetric flask and made up to volume with 60% dioxane. This solution was then placed in one of the reservoir syringes of a Durrum-Gibson stopped-flow spectrophotometer; the solution made up of the nucleophile, its conjugate acid, and lithium perchlorate was placed in the other reservoir syringe. The instrument was thermostated at 25°, and the reaction of **3** with the nucleophile was followed by monitoring the decrease in optical density with time, normally at 244 nm. With three nucleophiles it was necessary to use somewhat longer wavelength because of absorbance by the nucleophile at 244 nm. These (and the wavelength used) were: CH_3CONHO^- (258 nm); piperazine (260 nm); HO_2^- (270 nm).

For the runs followed by conventional spectrophotometry, 4 ml of the solution containing the nucleophile, its conjugate acid, and lithium perchlorate was placed in a 1-cm cell and thermostated at 25° in the cell compartment of a Perkin-Elmer Model 402 spectrophotometer. Once the solution had come to thermal equilibrium the reaction was initiated by adding and rapidly mixing 0.05 ml of a stock solution of **3** in dioxane with the solution already in the cell. The decrease in optical density with time was then followed. The wavelengths used for the different nucleophiles were as follows: 244 nm (CN^-, imidazole, glycine ethyl ester, and $H_3N^+CH_2CH_2CH_2$); 258 nm (piperazine H^+). Runs with glycine ethyl ester, where the rate was also followed by the stopped-flow procedure, showed that the rate constants for a given run as determined by the two different procedures were identical within experimental error.