

Correlation of Nucleophilicities toward Trivalent Nitrogen. Reactions of Hydroxylamine-*O*-sulfonate with Ethanethiolate, Hydroxylamine, and Hydroxide

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Abstract: Nucleophilic substitution on the nitrogen center in the hydroxylamine-*O*-sulfonate ion has been examined for $C_2H_5S^-$, $HONH_2$, and OH^- as nucleophiles. Each reaction obeys the rate expression $-d[H_2NOSO_3^-]/dt = k_2[H_2NOSO_3^-][Nu]$ with k_2 ($M^{-1} sec^{-1}$, 20°) equal to 32, 1.4×10^{-3} , and 2×10^{-5} for $C_2H_5S^-$, $HONH_2$, and OH^- , respectively. Diimine, $HN=NH$, is formed in both the hydroxylamine and the hydroxide reaction and an attempt was made to minimize its effect on the kinetics by means of scavenging with added fumarate ion. Combining the present results with those of earlier studies establishes an order of nucleophilicity toward trivalent nitrogen in $H_2NOSO_3^-$, $C_2H_5S^- \sim (C_6H_5)_3P > (H_2N)_2CS > ^-O_3SS^- > I^- (>Br^- > Cl^-) > (C_2H_5)_3N > HONH_2 > OH^-$, in which there is a range in reactivity of 10^6 . This order is qualitatively parallel with that established for sp^3 carbon, peroxide oxygen, and platinum(II) as electrophilic centers. The results suggest that for substitution on trivalent nitrogen in compounds of the type NH_2-X polarizability of the nucleophile plays a major role, with basicity making a minor contribution.

Characterizations of a variety of centers that undergo nucleophilic substitution, *e.g.*, platinum(II),² sulfur,³ peroxide oxygen,⁴ phosphorus,⁴ and boron,⁵ have appeared recently. In the case of trivalent (sp^3) nitrogen in compounds of the type NH_2X , kinetics of substitution for a single substrate, which would allow an order of nucleophilicity to be established, have not been available.^{6,7} Thus, the description by Edwards and Pearson⁸ of trivalent nitrogen as a relatively soft electrophilic center was supported largely by results of product studies.

As part of a study of substitution at trivalent nitrogen, we have reported the kinetics of reactions of hydroxylamine-*O*-sulfonic acid with a variety of soft base nucleophiles.⁹⁻¹¹ The $H_2NOSO_3^-$ ion reacts *via* mechanisms which have as a common feature initial rate-determining attack on nitrogen, with sulfate ion



as the leaving group. Presumably, structural features in the transition state for eq 1 closely resemble those for reactions of alkyl carbon substrates, with replacement of a C-H bond by a lone pair on nitrogen. In general, direct attack on nitrogen has been established by the isolation of products or intermediates with a nitrogen to donor atom bond, by the large negative activation entropies observed, and by the pronounced steric

retardation in reactions of $RHNOSO_3^-$ derivatives.^{9,10,12-14}

In this paper results for several basic nucleophiles are reported, which together with our earlier results make possible an evaluation of nucleophilicity toward trivalent nitrogen.

Experimental Section

Reagents and Syntheses. Hydroxylamine-*O*-sulfonic acid was prepared and analyzed as described previously;⁹ the purity of samples used was 97-99%. Reagent grade salts, hydroxylamine hydrochloride (Mallinckrodt), potassium perchlorate (used to maintain ionic strength), and the various salts for preparation of buffer solutions, were used as received after drying at 110° . MCB (99+%) fumaric acid, neutralized with NaOH, was employed in the hydroxide and hydroxylamine studies. Eastman yellow label ethanethiol was distilled using a nitrogen bleed and was subsequently stored and handled under prepurified nitrogen. Diethyl disulfide was prepared by iodine oxidation of ethanethiol. Several attempts to isolate ethylsulfenamide from a mixture of $>10^{-3}$ M concentrations of $C_2H_5S^-$ and $H_2NOSO_3^-$ resulted only in the formation of $C_2H_5SSC_2H_5$, which in nmr, and uv spectra showed to be identical with the disulfide prepared independently.¹⁵ 2-Sulfenamido-pyridine was prepared and recrystallized, using procedures described for chloramine,¹⁷ from 2-mercaptopyridine and hydroxylamine-*O*-sulfonic acid, mp $78-79^\circ$ ($79-80^\circ$ reported¹⁷).

Kinetics. Ethanethiolate reactions were monitored at 238 nm using a Cary Model 16K spectrophotometer. All solutions were prepared from doubly distilled water which had been thoroughly purged with prepurified nitrogen. A solution (3.00 ml) containing $H_2NOSO_3^-$ and NaOH was placed into a 1-cm cell, thermostated in the cell block. Using a syringe, a 0.200-ml quantity of a solution, prepared on a weight basis from ethanethiol and either water or

(1) NDEA Fellow, 1971-1973.

(2) L. Cattalini, *Progr. Inorg. Chem.*, **13**, 263 (1970).

(3) J. L. Kice, *Progr. Inorg. Chem.*, **17**, 147 (1972).

(4) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1964, Chapters 4 and 5.

(5) W. L. Budde and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 3147 (1971).

(6) A preliminary report of nucleophilic substitution on nitrogen in *O*-(2,4-dinitrophenyl)hydroxylamine has appeared very recently. S. Oae and F. Yamamoto, *Tetrahedron Lett.*, 5143 (1973).

(7) Oxidation of a series of nucleophiles by difluoramine has been interpreted in terms of substitution on nitrogen. W. T. Yap, A. D. Craig, and G. A. Ward, *J. Amer. Chem. Soc.*, **89**, 3442 (1967).

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

(9) J. H. Krueger, P. F. Blanchet, A. P. Lee, and B. A. Sudbury, *Inorg. Chem.*, **12**, 2714 (1973).

(10) P. F. Blanchet and J. H. Krueger, *Inorg. Chem.*, **13**, 719 (1974).

(11) B. A. Sudbury and J. H. Krueger, *Inorg. Chem.*, **13**, 1736 (1974).

(12) P. A. S. Smith, H. R. Alul, and R. L. Baumgarten, *J. Amer. Chem. Soc.*, **86**, 1139 (1964).

(13) In a recent report, an attempt to detect substitution on nitrogen in *N*-hydroxysuccinimide *O*-trifluoromethanesulfonate was unsuccessful, despite the presence of an excellent leaving group, presumably due to a steric, and possibly, an electronic effect arising from the $R(C=O)$ group. T. M. Chapman and E. A. Freedman, *J. Org. Chem.*, **38**, 3908 (1973).

(14) In contrast, however, Oae and Yamamoto reported that rates are not very sensitive to methyl groups adjacent to the donor atom in the attacking base.⁸

(15) Formation of the disulfide from a presumed sulfenamide intermediate has been reported for related systems.^{6,16}

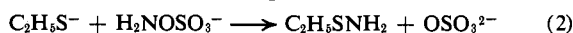
(16) H. H. Sisler, N. K. Kotia, and R. E. Highsmith, *J. Org. Chem.*, **35**, 1742 (1970).

(17) M. A. Robinson and T. H. Hurley, *Inorg. Chem.*, **4**, 1716 (1965).

aqueous sodium hydroxide, was rapidly injected into the reaction cell. Except in the fastest reactions, the cell was inverted several times to ensure thorough mixing. In all mixtures sufficient NaOH was present to maintain pH > 12.7, ensuring at least a 95% conversion to the $C_2H_5S^-$ form ($pK_a \cong 11.0$ for C_2H_5SH in water).¹⁸ The hydroxylamine and hydroxide reactions were carried out in a thermostated reaction flask from which samples were withdrawn and quenched with 0.1 *N* acetic or sulfuric acid. Residual hydroxylamine-*O*-sulfonic acid was analyzed iodometrically.

Results

Ethanethiolate-Hydroxylamine-*O*-sulfonate Reaction. Although $C_2H_5SNH_2$ was not detected as a product, the following results support eq 2 as the stoichiometric



change in the dilute solutions on which rate measurements were made. In a reaction mixture with $[C_2H_5S^-]_0 = [H_2NOSO_3^-]_0 = 0.89 \times 10^{-3} M$, the absorbance in the 230–250-nm region decreased rapidly to near zero (for $C_2H_5S^-$, ϵ 5300 $M^{-1} cm^{-1}$ at λ_{max} 238 nm). There was no significant production of $C_2H_5SSC_2H_5$, since its formation would have required $A = 0.16$ at λ_{max} 245 nm. When $[C_2H_5S^-]_0$ was doubled, A_{238} decreased rapidly to one-half its initial value, followed by a much slower further decrease; thus, only 1 mol of $C_2H_5S^-$ is consumed per mole of $H_2NOSO_3^-$. Attempts to isolate ethylsulfenamide from more concentrated mixtures led only to the recovery of diethyl disulfide. Aromatic sulfenamides are much more stable than alkyl sulfenamides and we did find that, like chloramine,¹⁷ $H_2NOSO_3^-$ reacts with 2-mercapto-pyridine to give 2-sulfenamidopyridine.

The kinetics of the reaction were measured following the decrease in absorbance of $C_2H_5S^-$ at 238 nm. Data were analyzed assuming eq 2 and the rate law

$$-d[C_2H_5S^-]/dt = k_2[H_2NOSO_3^-][C_2H_5S^-]$$

For the concentration ranges shown in Table I, the data

Table I. Kinetics of the Ethanethiolate-Hydroxylamine-*O*-sulfonate Reaction in Water^a

$10^4[H_2NOSO_3^-]_0$, <i>M</i>	$10^4[C_2H_5S^-]_0$, <i>M</i>	$[OH^-]$, <i>M</i>	$k_2(av)$, $M^{-1} sec^{-1}$
0.64–1.29	1.17–1.85	0.047	33.3 ± 1.2 (4) ^b
0.70–1.39	0.91–0.97	0.047	31.8 ± 1.5 (4)
1.21–2.42	1.14–1.48	0.094	32.0 ± 0.7 (2)
1.21	1.25	0.047	32.1 ± 0.7 (2)
7.5	1.6	0.051	30.1 ± 0.6 (3)
16.9	1.6	0.057	32.0 ± 1.3 (3)

^a At 20.3°, 0.100 *M* ionic strength. ^b Number of runs in the indicated concentration ranges.

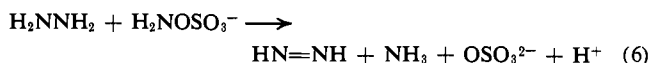
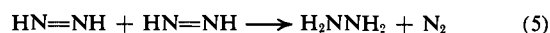
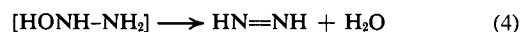
do conform accurately to a second-order rate law for at least two half-lives, with $k_2 = 32 \pm 2 M^{-1} sec^{-1}$. The rate constants obtained are independent of hydroxide ion concentration, indicating that OH^- does not compete with $C_2H_5S^-$ under the reaction conditions.

Reaction of Hydroxylamine with Hydroxylamine-*O*-sulfonate Ion. In a preliminary study of the reaction it was found that rates were quite nonreproducible, both among runs and also, in several cases, within a given run. Such behavior is not surprising, since some of the steps which have been suggested¹⁹ for this system, eq

(18) M. M. Kreevoy, E. T. Harper, R. E. Duvall, H. S. Wilgus, III, and L. T. Ditsch, *J. Amer. Chem. Soc.*, **82**, 4899 (1960).

(19) E. Schmitz, R. Ohme, and G. Kozakiewicz, *Z. Anorg. Allg. Chem.*, **339**, 44 (1965).

3–6, involve the highly reactive diimine molecule,



N_2H_2 .²⁰ $HONHNNH_2$ has not been detected, but there is good, though indirect, evidence for the formation of diimine,¹⁹ which subsequently forms the competing nucleophile, hydrazine. We found that reaction 6, which involves $H_2N-NH-NH_2$ as an intermediate,¹⁹ proceeds somewhat more rapidly than eq 3. Thus, $H_2NOSO_3^-$ will also be consumed *via* eq 6 at rates that depend on the conditions which control the diimine concentration. Since molecules containing activated double bonds are known to undergo fairly rapid cis hydrogenation by diimine,^{19,21,22} we felt that added fumarate ion would scavenge diimine, thereby eliminating complicating reactions that arise from its presence. As expected, addition of increasingly higher concentrations of fumarate led to substantially lower and less erratic rates.

Rate measurements were carried out in 0.050 *M* fumarate solutions and the data were analyzed assuming the 1:1 stoichiometry of eq 3 and the rate law

$$-d[H_2NOSO_3^-]/dt = k_2[H_2NOSO_3^-][HONH_2]$$

(Table II). Plots of $\ln([HONH_2]/[H_2NOSO_3^-])$ vs. t

Table II. Kinetics of the Reaction between Hydroxylamine and the Hydroxylamine-*O*-sulfonate Ion at 20°^a

$10^4[H_2NOH]_0$, <i>M</i>	$10^4[H_2NOSO_3^-]_0$, <i>M</i>	μ , <i>M</i>	10^4k_2 , $M^{-1} sec^{-1}$
2.50	5.00	0.53	1.8
2.50	5.00	0.53	1.5
2.50	5.00	0.53	1.1
2.50	4.87	0.53	1.3
5.0	2.50	0.53	1.7
7.5	2.50	0.28	1.7
10.0	1.09	0.74	0.7
4.06	4.06	3.52	1.5 ^b
2.50	5.00	0.10	1.4 ^c

^a All solutions contained a HCO_3^- - CO_3^{2-} buffer and 0.050 *M* sodium fumarate, except as noted. ^b With 0.50 *M* sodium fumarate. ^c Boric acid-borate buffer. No fumarate present.

were linear for the extent of reaction studied, *ca.* 1.5 half-lives. Apparently, most of the diimine is scavenged in the 0.05 *M* fumarate solutions, since an increase in the fumarate concentration to 0.50 *M* did not further decrease the rate. Thus, the rate constants in Table II correspond to eq 3 as the rate-determining step, although it is doubtful that the rate effects arising from diimine have been eliminated entirely. The average value of $k_2 = (1.4 \pm 0.4) \times 10^{-3} M^{-1} sec^{-1}$ obtained is close to values of 1×10^{-3} ¹⁹ and 0.6×10^{-3} ,²¹ taken from

(20) The involved nature of the analogous chloramine reaction in liquid ammonia has been discussed. F. N. Collier, Jr., H. H. Sisler, J. G. Calvert, and F. R. Hurley, *J. Amer. Chem. Soc.*, **81**, 6177 (1959).

(21) W. Dürckheimer, *Justus Liebigs Ann. Chem.*, **721**, 240 (1969).

(22) (a) S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem., Int. Ed. Engl.*, **4**, 271 (1965); (b) C. E. Miller, *J. Chem. Educ.*, **42**, 254 (1965).

results of limited rate measurements which have been reported. The agreement is somewhat surprising since scavenging was not employed in the earlier work.

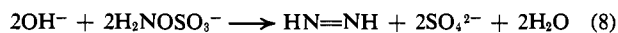
In the pH 9–11 range examined, there was no discernible hydroxide ion dependence, which eliminates deprotonation of $\text{H}_2\text{NOSO}_3^-$ as an important step in the mechanism.²³ In acidic solutions in which hydroxylamine is protonated, no reaction takes place.

When boric acid–borate buffer solutions without added fumarate were used, rates were reasonably reproducible and the rate constants observed were close to those found for fumarate solutions. This apparent scavenging ability by the buffer would arise if boric acid, like fumarate, were reduced by diimine, possibly to $\text{HB}(\text{OH})_2$.²⁴

Hydroxide–Hydroxylamine-*O*-sulfonate Reaction. This reaction proceeds according to eq 7 at approxi-



mately 5% of the rate of the $\text{HONH}_2\text{--H}_2\text{NOSO}_3^-$ reaction. The hydroxylamine formed in eq 7 must undergo further rapid reaction as shown in eq 3–6, thus making scavenging of diimine necessary. Rate measurements were carried out in 0.05 *M* fumarate solutions in which the stoichiometry in eq 8 will apply in the limit of



complete scavenging of diimine. Rates measured with added 0.05 *M* succinate (no scavenging, but with a medium effect similar to that of fumarate) were 10–15% higher.

Second-order constants were calculated from the rate data assuming the 1:1 stoichiometry in eq 8 and the rate law

$$-d[\text{H}_2\text{NOSO}_3^-]/dt = k_2[\text{H}_2\text{NOSO}_3^-][\text{OH}^-]$$

Good linearities in the appropriate $\ln [\text{H}_2\text{NOSO}_3^-]$ vs. t or $\ln ([\text{H}_2\text{NOSO}_3^-]/[\text{OH}^-])$ vs. t plots were obtained over the extent of reaction examined, two or three half-lives. With 0.050 *M* fumarate added and $[\text{H}_2\text{NOSO}_3^-]_0 = 0.021$ *M*, $10^5 k_2$ ($M^{-1} \text{sec}^{-1}$, 20.0°, $\mu = 1.10$ *M*) was 7.6, 7.0, 6.9, and 7.7 (av 7.3) for $[\text{OH}^-]_0$ of 0.156, 0.339, 0.52, 0.89 *M*, respectively.²⁵

The rate law observed is consistent with hydroxide attack on any one of the centers (a) nitrogen, (b) hydrogen, or (c) sulfur. A study of the alkaline hydrolysis of $\text{H}_2\text{NOSO}_3^-$ in H_2^{18}O indicated complete N–O cleavage,²⁷ ruling out the possibility of significant attack on the sulfonate sulfur. Deprotonation by hydroxide to HNOSO_3^{2-} , process b, prior to loss of sulfate cannot be ruled out. However, evidence favoring substitution on nitrogen has been presented for analogous chloramine reactions.²⁸

(23) Deprotonation to HNOSO_3^{2-} , followed by dissociation to nitrene, NH , occurs only at pH >13, if at all.¹⁹ R. Appel and W. Büchner, *Justus Liebigs Ann. Chem.*, **654**, 1 (1962); G. Yagil and M. Anbar, *J. Amer. Chem. Soc.*, **84**, 1797 (1962).

(24) A $\text{HB}(\text{OH})_2$ species has been suggested to account for results of low-temperature hydrolyses of diborane in ethanol–water media. W. L. Jolly and T. Schmitt, *J. Amer. Chem. Soc.*, **88**, 4282 (1966).

(25) Stability studies of $\text{H}_2\text{NOSO}_3^-$ in alkaline solution have been reported and, from the single run available in each case, the following were calculated: $k_2 = 7 \times 10^{-5} M^{-1} \text{sec}^{-1}$ (20°, $\mu = [\text{OH}^-]_0 = 0.5$ *M*)¹⁹ and $k_2 = 3 \times 10^{-5} M^{-1} \text{sec}^{-1}$ (23°, $\mu = 0.2$ *M*, $[\text{OH}^-]_0 = 0.12$ *M*).²⁶

(26) H. J. Matsuguma and L. F. Audrieth, *J. Inorg. Nucl. Chem.*, **12**, 186 (1959).

(27) J. P. Candlin and R. G. Wilkins, *J. Amer. Chem. Soc.*, **87**, 1490 (1965).

For purposes of comparison with results obtained for other nucleophiles, k_2 for the $\text{OH}^- \text{--} \text{H}_2\text{NOSO}_3^-$ reaction is taken to be $2 \times 10^{-5} M^{-1} \text{sec}^{-1}$ at $\mu = 0.10$ *M*. The observed second-order rate constants must be divided by two since they refer to loss of two $\text{H}_2\text{NOSO}_3^-$ for each initial rate-determining attack on $\text{H}_2\text{NOSO}_3^-$. In addition, the rate constant for an ionic strength of 0.10 *M* is estimated to be approximately one-half the value obtained at $\mu = 1.10$ *M*.²⁹

Discussion

The second-order rate constants are summarized in Table III together with results reported previously.^{9,10}

Table III. Second-Order Rate Constants for Reaction of Hydroxylamine-*O*-sulfonic Acid. Nonkinetic Properties of the Nucleophiles

Nucleophile	k_{Nu} , $M^{-1} \text{sec}^{-1}$ ^a	$5 + \log k_{\text{Nu}}$	E_a ^c	H^e, h	pK CH_3Hg^+ ⁱ
$\text{C}_2\text{H}_5\text{S}^-$	32	6.51	3 ^f	12.7	16
$(\text{C}_6\text{H}_5)_3\text{P}$	1.96 ^{b, c}	5.29		4.4	9.2
$(\text{H}_2\text{N})_2\text{CS}$	1.64 ^d	5.21	2.18	0.7	7
$-\text{O}_3\text{SS}^-$	0.55 ^d	4.74	2.52	3.6	11.0
I^-	0.069 ^b	3.84	2.06	−9	8.7
$(\text{C}_2\text{H}_5)_3\text{N}$	0.022 ^b	3.34		12.4	
HONH_2	0.0014	2.15		7.5	
OH^-	2×10^{-4}	0.3	1.7 ^g	17.5	9.4

^a In water, 20°, 0.10 *M* ionic strength. ^b Reference 9. ^c Obtained in 50.0 weight % methanol–water. In water, the value is estimated to lie in the range 20–100 $M^{-1} \text{sec}^{-1}$.¹¹ ^d Reference 10. ^e In the Edwards equation, $\log (k_{\text{Nu}}/k_{\text{H}_2\text{O}}) = \alpha E_a + \beta H$, $E_a = E^0 + 2.60$ V for $2\text{Nu}^- \rightleftharpoons \text{Nu}_2 + 2e^-$ and $H = 1.74 + \text{p}K_a(\text{NuH}^+)$. J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954). ^f Taken to be the value calculated using the oxibase equation for reaction of $\text{H}_2\text{NCH}_2\text{CH}_2\text{S}^-$ with CH_3I . R. E. Davis, S. P. Molnar, and R. Nehring, *J. Amer. Chem. Soc.*, **91**, 97 (1969). ^g W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Englewood Cliffs, N. J., 1952, p 45. ^h R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968). ⁱ pK for dissociation of CH_3HgNu . G. Schwarzenbach and M. Schellenberg, *Helv. Chim. Acta*, **48**, 28 (1965). Values for $\text{C}_2\text{H}_5\text{S}^-$ and $(\text{C}_6\text{H}_5)_3\text{P}$ are estimates based on results for $\text{HOCH}_2\text{CH}_2\text{S}^-$ and $(\text{C}_6\text{H}_5)_2(m\text{-C}_6\text{H}_4\text{SO}_3^-)\text{P}$, respectively.

All values were obtained under uniform conditions of solvent,³⁰ temperature, and ionic strength and refer to attack on nitrogen in $\text{H}_2\text{NOSO}_3^-$. The overall order of nucleophilicity observed is $\text{C}_2\text{H}_5\text{S}^- \sim (\text{C}_6\text{H}_5)_3\text{P} > (\text{H}_2\text{N})_2\text{CS} > -\text{O}_3\text{SS}^- > \text{I}^- (> \text{Br}^- > \text{Cl}^-) > (\text{C}_2\text{H}_5)_3\text{N} > \text{HONH}_2 > \text{OH}^-$. This order is one of decreasing softness of the nucleophiles and suggests that trivalent nitrogen is a predominantly soft electrophilic center.³¹ That soft bases react with particular advantage at trivalent nitrogen is expected, based on the presence of one lone pair and three bond pairs of electrons on nitrogen. The spread in rates of 10^6 indicates a substantial degree

(28) (a) M. Anbar and G. Yagil, *J. Amer. Chem. Soc.*, **84**, 1790 (1962); (b) W. J. le Noble, *Tetrahedron Lett.*, 727 (1966); (c) R. E. McCoy, *J. Amer. Chem. Soc.*, **76**, 1447 (1954).

(29) Value is based on ionic-strength effect results from ref 9 for the $\text{I}^- \text{--} \text{H}_2\text{NOSO}_3^-$ reaction, which is of the same charge type.

(30) Results for triphenylphosphine were obtained in 50.0 wt % methanol–water. See footnote c, Table III.

(31) According to the HSAB principle,³² the donor atom in a soft base possesses high polarizability, low electronegativity, and is readily oxidized. Alternatively, in terms of C_B (covalent) and E_B (ionic) parameters,³³ a large value of the ratio C_B/E_B indicates that softness is important in the interactions of a particular base.

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

(33) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, **93**, 6014 (1971).

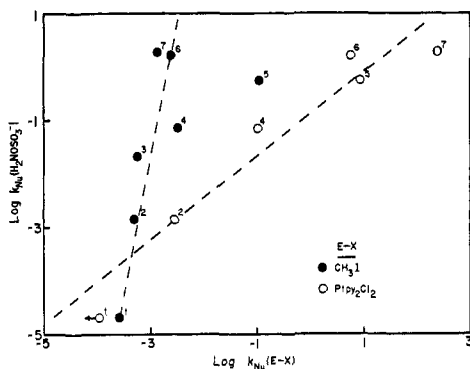
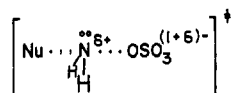


Figure 1. Plots of $\log k_{\text{Nu}}(\text{E-X})$ vs. $\log k_{\text{Nu}}(\text{H}_2\text{NOSO}_3^-)$, where E-X is $\text{CH}_3\text{-I}$ or $\text{Pt}(\text{py})_2\text{Cl-Cl}$. Data from Tables III and IV for nucleophiles: 1, OH^- ; 2, HONH_2 ; 3, $(\text{C}_6\text{H}_5)_3\text{N}$; 4, I^- ; 5, $\text{S}_2\text{O}_3^{2-}$; 6, $(\text{H}_2\text{N})_2\text{CS}$; 7, $(\text{C}_6\text{H}_5)_3\text{P}$.



of nucleophile–nitrogen bond formation. In addition, the significant N–O stretching depicted above is supported by results of solvent effect studies on reactions of $\text{H}_3\text{NOSO}_3^-$.¹¹

Increasing proton basicity of the leaving group decreases reactivity of H_2NX substrates. Thus, Oae and Yamamoto⁶ found $k = 0.023 \text{ M}^{-1} \text{ sec}^{-1}$ for reaction of triphenylphosphine with the anion of 2,4-dinitrophenol ($\text{p}K_a = 4.0$) as the leaving group. In dimethyl sulfide, OSO_3H^- is a much better leaving group than is OSO_3^{2-} .^{11,34}

Also shown in Table III are values of several non-kinetic quantities which have been used to correlate reactivity at other electrophilic centers. As in the case of sp^3 carbon, there does appear to be a correlation between $\log k_{\text{Nu}}$ and E_n values in the Edwards³⁶ or oxibase equation³⁷ but no correlation at all with H . The $\text{p}K$ values for CH_3Hg^+ , which has been suggested as a reference soft acid,³⁸ do not appear to provide a useful correlation for reaction of $\text{H}_2\text{NOSO}_3^-$.

Figure 1 and Table IV provide a comparison with results for kinetics of substitution at other electrophilic centers. The sp^3 nitrogen center responds to the nucleophiles in a fashion that parallels the response of sp^3 carbon (a moderately soft center) and peroxide oxygen

(34) Preliminary studies on *O*-mesitylenesulfonylhydroxylamine³⁵ indicate that this substrate is far more reactive toward several of the nucleophiles than is $\text{H}_2\text{NOSO}_3^-$.

(35) L. A. Carpino, *J. Amer. Chem. Soc.*, **82**, 3133 (1960).

(36) J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954).

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Table IV. Comparison of Relative Nucleophilic Reactivities

Nucleophile	$\text{sp}^3 \text{ C}$ CH_3I^a $k_{\text{Nu}}/k_{\text{I}}$	$\text{sp}^3 \text{ N}$ $\text{H}_2\text{NOSO}_3^-$ $k_{\text{Nu}}/k_{\text{I}}$	Peroxide O, H_2O_2^b $k_{\text{Nu}}/k_{\text{I}}$	Pt(II) $\text{Pt}(\text{py})_2\text{Cl}_2^c$ $k_{\text{Nu}}/k_{\text{I}}$
$\text{C}_2\text{H}_5\text{S}^-$	[600] ^d	460	3.3 ^f	
$(\text{C}_6\text{H}_5)_3\text{P}$	0.38	>28 ^e		2300
$(\text{H}_2\text{N})_2\text{CS}$	0.70	24		60
$\text{S}_2\text{O}_3^{2-}$	33	8	2.5	80
I^-	1.00	1.00	1.00 ^g	1.00
$(\text{C}_6\text{H}_5)_3\text{N}$	0.17	0.32	0.033	
HONH_2	0.15	0.020		0.027
OH^-	~0.07	0.0003	Very small	Very small

^a Data for $\text{Nu} + \text{CH}_3\text{I} \rightarrow \text{CH}_3\text{Nu} + \text{I}^-$ at 25 or 30° in methanol.³⁸

^b Data from ref 4, p 77, for oxidation of nucleophiles by H_2O_2 in water at 25°. ^c Data for $2\text{Nu} + \text{Pt}(\text{py})_2\text{Cl}_2 \rightarrow \text{Pt}(\text{py})_2\text{Nu}_2 + 2\text{Cl}^-$ in methanol at 25°. ^d Based on $k_2 = 2.1 \text{ M}^{-1} \text{ sec}^{-1}$ for reaction of $\text{H}_2\text{NCH}_2\text{CH}_2\text{S}^-$ with CH_3I in water. See footnote f, Table III. ^e Lower limit. See footnote c, Table III. ^f Based on $k_2 = 0.033 \text{ M}^{-1} \text{ sec}^{-1}$ (estimated using the oxibase equation) for reaction of H_2O_2 with $\text{H}_2\text{NCH}_2\text{CH}_2\text{S}^-$. See footnote f, Table III. ^g Values based on $k_1 = 0.010 \text{ M}^{-1} \text{ sec}^{-1}$ (H. A. Liebhassky and A. Mohammad, *J. Amer. Chem. Soc.*, **55**, 3977 (1933)).

and platinum(II) (very soft centers). Figure 1 shows that the discrimination among nucleophiles (*i.e.*, the slopes approximated in the figure) by nitrogen in $\text{H}_2\text{NOSO}_3^-$ is comparable with that shown by $\text{Pt}(\text{py})_2\text{Cl}_2$ and somewhat greater than that for CH_3I . Although it illustrates the similarity in response of the electrophilic centers, Figure 1 is not intended to express a quantitative relationship between the rate constants since the atom centers undergoing reaction are inherently somewhat different, the leaving groups are different, and the data for CH_3I and $\text{Pt}(\text{py})_2\text{Cl}_2$ refer to solvent methanol.³⁹

Trivalent nitrogen appears to be intermediate in character between sp^3 carbon and Pt^{II} or oxygen. For example, OH^- is essentially unreactive toward platinum(II) or peroxide-oxygen, has a low but measurable reactivity toward nitrogen, and reacts fairly rapidly with sp^3 carbon. Among the nucleophiles with a sulfur donor atom, $\text{C}_2\text{H}_5\text{S}^-$, which is both polarizable and strongly basic, has a considerably greater reactivity than $\text{S}_2\text{O}_3^{2-}$ or $(\text{H}_2\text{N})_2\text{CS}$. Thus, our results support the earlier prediction by Edwards and Pearson that in substitution on compounds of the type NH_2X , polarizability of the nucleophile plays a major role, with basicity making a minor contribution to reactivity.

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(39) The most extensive set of data was available in this solvent. Results for OH^- are uncertain since its reactivity is markedly dependent on the solvent and leaving group. The OH^- value for CH_3I is approximated from the rate constant for CH_3O^- . The OH^- point for $\text{Pt}(\text{py})_2\text{Cl}_2$ is an upper limit only.