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Nucleophilic Substitution on Nitrogen. Kinetics of Reactions of Hydroxylamine-*O*-sulfonate Ion

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Kinetics of the reactions of hydroxylamine-*O*-sulfonate ion, $H_2NOSO_3^-$, with the nucleophiles I^-, $(C_6H_5)_3P$, and $(C_2H_5)_3N$ have been measured in water and in 50 wt % methanol–water. For each reaction a rate law of the type $-d[H_2NOSO_3^-]/dt = k_2[H_2NOSO_3^-][Nu]$ was observed. The mechanism proposed for each system involves nucleophilic substitution on the nitrogen atom, with SO_4^{2-} as the leaving group. The order of nucleophilicities observed is $(C_6H_5)_3P > I^- > (C_2H_5)_3N \gg Br^-, Cl^-$. A significant result is the decrease in reactivity of $H_2NOSO_3^-$ upon protonation of the nitrogen lone pair to form molecular H_3NOSO_3. Deuterium isotope effects observed for reaction of $H_2NOSO_3^-$, compared with $D_2NOSO_3^-$ in D_2O, are $k_H/k_D = 1.5$ for $(C_6H_5)_3P$ and 1.3 for I^-. Replacement of H by CH_3 or $C_6H_5C(O)$ greatly decreases reactivity, suggesting a large steric influence in the transition state.

Introduction

Factors that influence rates of substitution at inorganic atom centers have been the subject of a number of recent studies.[2] These studies have led to detailed characterizations of several centers, notably Pt^{II} in square-planar complexes,[2,3] sulfur in the II, IV, and VI oxidation states,[4] peroxide oxygen,[2] and phosphorus.[2] However, there has been no systematic kinetic investigation of the trivalent (sp^3) nitrogen center, although a number of reactions have been interpreted in terms of substitution on nitrogen.[2,5] Recent rate studies include hydrolysis and iodide ion reduction of *N*-substituted hydroxylamine-*O*-sulfonic acids,[6] reactions of coordinated hydroxylamine-*O*-sulfonate,[7] reactions of anions with HNF_2[8] and with NF_3,[9] SN2 reactions of chloramines,[10] and substitution on the sp^2 nitrogen in $C(NO_2)_4$.[11]

The hydroxylamine-*O*-sulfonate anion appeared to us to be an especially promising reactant on which to carry out a detailed study of nucleophilic substitution at trivalent nitrogen. The general properties,[12] structure,[13] and hydrolysis reactions[14] of the stable, solid acid, H_3NOSO_3, have been described. Our objective was to study the kinetics of reaction of $H_2NOSO_3^-$ with a wide range of nucleophiles under a uniform set of conditions, assuming eq 1 as a general model

$$Nu + H_2N\text{-}OSO_3^- \rightarrow Nu\text{-}NH_2^+ + SO_4^{2-} \qquad (1)$$

for the rate-determining step. We report here results for several nucleophiles, including the consequences of protonation of the nitrogen lone pair and replacement of H by CH_3 and by deuterium.

Experimental Section

Solvents and Reagents. Doubly distilled water and B & A reagent grade methanol were used throughout. Work with iodide at low pH was carried out in N_2-purged solvents. Reagent grade salts were dried before use. Triphenylphosphine was recrystallized from cyclohexane (mp 80°) and *N*-methylhydroxylamine hydrochloride was recrystallized from methanol, including treatment with activated carbon and precipitation with ether. MCB triethylamine (100 ± 0.5% by titration) was used as received. Deuterated solvent runs were made in D_2O (Stohler, 99.8%) and in CH_3OD (Stohler, 99%, *vide infra*).

Synthetic Procedures. Hydroxylamine-*O*-sulfonic acid was prepared by a modification of the method of Sommer, *et al.*[15] Hydroxylammonium sulfate was added to a fivefold excess of chlorosulfonic acid and the reaction mixture was stirred for 30 min at 100°. The product was precipitated and washed with cold, dry ether and then dried *in vacuo* over P_2O_5. Contact with moist air was minimized to prevent hydrolysis. Satisfactory purity (96–98%) was attained without recrystallization. Over a period of weeks the acid slowly hydrolyzed to hydroxylammonium sulfate. Only samples with greater than 94% purity were used for kinetic runs and the per cent purity was used in calculating the concentration values reported. Samples were analyzed iodometrically, based on eq 2. The preferred analytical conditions involve use of excess potassium iodide, pH 3, and reaction times of 5–10 min. Although identical results were obtained using highly acidic solutions, as suggested in the standard analytical procedure,[16] the use of strong acid offers no advantage in rate and can result in concomitant air oxidation.

N-Methylhydroxylamine-*O*-sulfonic acid was prepared from *N*-methylhydroxylamine hydrochloride as described above. The product proved to be quite stable when protected from moisture. Because hydrolysis of the acid occurs at a rate comparable with the very low rate of reaction with iodide, iodometric analysis is not feasible. The equiv wt 124.6 (calcd 127.1) was found by NaOH titration. *Anal.* Calcd for CH_5NO_4S: C, 9.45; H, 3.96; S, 25.2. Found: C, 9.36; H, 4.02; S, 25.5.

Aminotriphenylphosphonium hydrogen sulfate, $(C_6H_5)_3PNH_2^+HSO_4^-$, was synthesized from triphenylphosphine and hydroxylamine-*O*-sulfonic acid.[17] *Anal.* Calcd for $C_{18}H_{18}NO_4PS$: C, 57.7; H, 4.84; N, 3.74. Found: C, 57.7; H, 4.69; N, 3.80.

Kinetics. Reactions with iodide and triphenylphosphine were

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followed using a Cary Model 16K spectrophotometer. Previously thermostated reactant solutions were rapidly mixed and aliquots transferred to 1-cm glass-stoppered silica cells. The cell-block turret and the outer sample compartment were thermostated to ±0.1°. Buffer solutions containing the hydroxylamine-*O*-sulfonate anion were prepared in the appropriate solvent from perchloric acid, solid H_3NOSO_3, and sodium acetate. Sodium perchlorate was employed to maintain constant ionic strength, usually at 0.100 *M*. Pseudo-first-order rate constants were calculated from absorbance data using a least-squares program, KINDAT.[18]

The reaction of iodide with hydroxylamine-*O*-sulfonic acid was followed by measuring the absorbance at 400 nm of triiodide ion. Consumption of iodine by solvent impurities (in methanol–water) and air oxidation of iodide were negligible. In determining the stoichiometry of the reaction, the iodine produced was titrated with standardized $Na_2S_2O_3$, followed by NaOH titration of the hydrogen ion remaining.

Reactions of triphenylphosphine (ϵ_{260} 11,500 M^{-1} cm^{-1}) were followed by monitoring the decrease in absorbance at 260 nm in 50.0 wt % methanol–water. Several runs at 280 nm, with higher triphenylphosphine concentrations, gave identical results. In the deuterated solvent, CH_3OD–D_2O, trace amounts of formaldehyde reacted with $H_2NOSO_3^-$, forming $CH_2{=}NOSO_3^-$.[15] Accordingly, CH_3OD was treated with sodium methoxide and iodine for 12 hr, followed by acidification, removal of excess iodine with thiosulfate, and distillation. No difficulty with impurities was encountered with reagent grade CH_3OH.

For reactions of triethylamine and hydroxylamine-*O*-sulfonate ion, previously thermostated solutions were rapidly mixed and allowed to react at 20°. Varying concentrations of NaOH were employed to neutralize H_3NOSO_3 and generate free amine. Ionic strength was adjusted to 0.100 *M* with potassium perchlorate. Aliquots were withdrawn periodically and quenched with cold, dilute H_2SO_4 containing excess KI. After 5 min, the iodine produced was titrated with $Na_2S_2O_3$. A blank run showed that there was no significant change in $H_2NOSO_3^-$ concentration, due to hydrolysis, even under the most basic conditions employed.

Results

Iodide–Hydroxylamine-*O*-sulfonate Reaction. The stoichiometry of the reaction

$$H_2NOSO_3^- + 3I^- + 2H^+ \rightarrow I_3^- + NH_4^+ + SO_4^{2-} \qquad (2)$$

was verified in both perchloric acid and acetate buffer solution (moles H^+ consumed/moles I_3^- produced) = 2.00 ± 0.02. Also, in the kinetic runs, infinite time absorbances at 400 nm were in good agreement (1–2%) with those expected on the basis of $\epsilon_{400}(I_3^-) = 5950\ M^{-1}\ cm^{-1}$ and $K_{dis}(I_3^-) = 0.00115$.[19]

Kinetic runs were carried out in a series of buffer solutions in which iodide was in large excess over hydroxylamine-*O*-sulfonate. Plots of ln $(A_\infty - A)$ *vs.* time were linear over the extent of reaction followed (3–4 half-lives), indicating a first-order dependence on $H_2NOSO_3^-$. Table I summarizes results for a series of runs at pH 4.75 in which pseudo-first-order rate constants were determined for a range of $[I^-]_0$. In the accessible range of iodide concentrations, the rate law $d[I_3^-]/dt = k_2[H_2NOSO_3^-][I^-]$ is obeyed within experimental error. Values of k_2 were independent of pH over the range 3.0–7.8 (Table I). The k_2 values are also independent of acetate concentration (10^{-3}–10^{-2} *M*), indicating that, if it occurs at all, base anion attack on $H_2NOSO_3^-$ is slow compared with the iodide reaction. Thus, the rate constants were taken to correspond to the iodide–$H_2NOSO_3^-$ reaction with $k_2 = 0.069 \pm 0.004\ M^{-1}\ sec^{-1}$ at 20.4°. At pH 4.75 and 10.4°, $k_2 = 0.031 \pm 0.001_5\ M^{-1}\ sec^{-1}$ and at 29.7°, $k_2 = 0.123 \pm 0.002\ M^{-1}\ sec^{-1}$, from which values of $\Delta H^\ddagger = 11.6 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -24 \pm 2$ eu were calculated from transition-state theory. As expected for the observed rate law, values of k_2 increased with increasing ionic strength; $k_2 = 0.053$ (0.021 *M*) and 0.080 $M^{-1}\ sec^{-1}$ (0.30 *M*). In 50.0 wt % methanol–water, k_2 was 0.037 $M^{-1}\ sec^{-1}$ at 20.4°.

Table I. Kinetic Data for the Reaction of Iodide Ion with Hydroxylamine-*O*-sulfonate Ion at 20.4° and 0.1 *M* Ionic Strength[a]

$10^2[I^-]_0$, *M*	10^2k_2, M^{-1} sec^{-1}	pH
2.00	7.0 (2)[b]	2.96 (1.00 × 10^{-3} *M* $HClO_4$)
4.00	7.0 (2)	
0.75	6.9	4.75 (HOAc–OAc^-)[c]
1.00	6.4	
1.50	6.7 (7)	
1.50	5.3 (2)[d]	
2.00	6.3 (2)	
3.00	6.6 (4)	
4.00	6.6 (2)	
6.00	7.1 (3)	
9.00	7.3 (2)	
1.50	7.1 (3)	5.35 (HOAc–OAc^-)[c]
2.00	6.6	5.65 (HOAc–OAc^-)[e]
4.00	7.0	
1.50	7.1	6.41 ($H_2PO_4^-$–HPO_4^{2-})[f]
1.50	7.4 (3)	7.21
2.00	6.9	7.76 (THAM)[g]
4.00	7.5	

[a] 1.00 × 10^{-4} *M* $H_2NOSO_3^-$. [b] Number of runs. [c] 4.0 × 10^{-3} *M* ΣOAc. [d] 99.8% D_2O. [e] 5.0 × 10^{-2} *M* ΣOAc. [f] 4.5 × 10^{-3} *M* ΣHPO_4. [g] 0.06 *M* $\Sigma(HOCH_2)_3CNH_2$.

Table II. Kinetic Data for the Iodide–Hydroxylamine-*O*-sulfonic Acid Reaction in Acid at 20.4° and 0.1 *M* Ionic Strength[a]

$10^2[H^+]_0$, *M*[b]	10^2k_2(obsd), M^{-1} sec^{-1}	$10^2[H^+]_0$, *M*	10^2k_2(obsd), M^{-1} sec^{-1}
1.01	6.29	4.22	5.03
1.01	6.11	4.28	4.89
2.00	5.74	4.23	3.09[c]
2.00	5.49	4.29	3.12[c]
2.54	5.47	5.08	4.81
3.01	5.22	5.08	4.43
3.01	5.28 (0.02 *M* I^-)	8.42	4.11
3.01	5.13 (0.03 *M* I^-)	8.54	3.99

[a] 1.00 × 10^{-4} *M* ΣH_3NOSO_3 and 1.50 × 10^{-2} *M* I^-. [b] Adjusted with $HClO_4$. [c] 99.8% D_2O.

Protonation of $H_2NOSO_3^-$ becomes important below pH 3 and is extensive at pH 1. Values of the second-order constant $k_2(\text{obsd}) = k_1/[I^-]_0$ were determined as a function of added $HClO_4$ (Table II). A rate law of the form $-d\Sigma[H_2NOSO_3^-]/dt = k_2[H_2NOSO_3^-][I^-] + k_{HOS}[H_3NOSO_3][I^-]$ was assumed to correlate the data, leading to eq 3, where K_{HOS} is the dissociation constant of hydroxylamine-*O*-sulfonic acid (HOS).

$$k_2(\text{obsd}) = \frac{k_2}{1 + [H^+]/K_{HOS}} + \frac{k_{HOS}}{1 + K_{HOS}/[H^+]} \qquad (3)$$

With $k_2 = 0.069\ M^{-1}\ sec^{-1}$ from Table I, the desired constants k_{HOS} and K_{HOS} were evaluated from a rearranged form of eq 3, $k_2(\text{obsd}) = k_{HOS} + K_{HOS}[k_2 - k_2(\text{obsd})]/[H^+]$. A plot of k_2(obsd) *vs.* $[k_2 - k_2(\text{obsd})]/[H^+]$ was linear for the data in Table II, although there was some scatter due to the rather small spread in rates involved. A least-squares fit gave $k_{HOS} = 0.023 \pm 0.003\ M^{-1}\ sec^{-1}$ and $K_{HOS} = 0.055 \pm 0.01$, the latter value being in reasonable agreement with a recent literature report of 0.033 (45°, $\mu = 1.0$ *M*).[14] Smith, *et al.*,[6] studied the H_3NOSO_3-I^- reaction under different conditions (0.1–2.0 *M* H^+ at 1.2°), so that a comparison of the kinetic results is

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difficult. They reported a second-order rate constant, in effect k_2(obsd), in 0.1 *N* HI that is consistent with the data in Table II.[20]

Added Cl^- and Br^- did not catalyze the reaction. With $[H^+] = 1.43 \times 10^{-3}$ *M* and $[I^-] = 7.5 \times 10^{-3}$ *M*, addition of 37.5×10^{-3} *M* Br^- had no effect on the rate, within experimental error. Assuming a possible additional term in the rate law of the type $k_{2(Br^-)}[Br^-]$, an upper limit of $k_{2(Br^-)}/k_{2(I^-)} \simeq 0.02$ can be placed on the nucleophilic reactivity of Br^-.[21]

Rate constants were also obtained in 99.8% D_2O (Tables I and II). At pH 4.75 where k_2 is a measure solely of the reaction of $H_2NOSO_3^-$, $k_H/k_D = 1.3 \pm 0.1$. Because amine-type hydrogens are known to exchange rapidly in moderately acidic to basic solutions,[22] it was assumed that k_2 measured in D_2O (k_D) corresponds to reaction of $D_2NOSO_3^-$.[23]

Triphenylphosphine–Hydroxylamine-*O*-sulfonate Reaction. In 50 wt % methanol-water at 20°, the reaction proceeds according to eq 4. The product aminotriphenylphosphonium

$$(C_6H_5)_3P + H_2NOSO_3^- \rightarrow (C_6H_5)_3PNH_2^+ + SO_4^{2-} \tag{4}$$

cation is the well-characterized, moderately stable species, reported earlier by Sisler, *et al.*,[24] and by Appel, *et al.*[17] The stoichiometry in eq 4 has been verified by two methods. First, triphenylphosphine (0.041 *M*) and hydroxylamine-*O*-sulfonic acid (0.047 *M*) were allowed to react to completion in methanol to yield a solid with properties and elemental analysis identical with those of an authentic sample of $(C_6H_5)_3PNH_2^+HSO_4^-$.[17] Second, the average value of the observed infinite time absorbances leads to a molar absorption coefficient for the product species of 2390 ± 210 M^{-1} cm^{-1} at 260 nm. This result is consistent with the value of 2300 found for known $(C_6H_5)_3PNH_2^+HSO_4^-$. A molar absorption coefficient of 1420 M^{-1} cm^{-1} is expected for triphenylphosphine oxide, thus ruling out any significant formation of this product. This result is consistent with the observation that $(C_6H_5)_3PNH_2^+$ is stable in dilute aqueous solution and undergoes appreciable hydrolysis to the oxide only at elevated temperatures.[24a,25]

Kinetic runs were carried out in acetate buffer solutions in 50 wt % methanol-water with $[H_2NOSO_3^-]_0/[(C_6H_5)_3P]_0$ in the range 13–40. The reaction was first order in triphenylphosphine, based on plots of ln $(A - A_\infty)$ *vs.* time that were linear for 2 or more half-lives. Pseudo-first-order rate constants were measured for a variety of initial hydroxylamine-*O*-sulfonate concentrations, leading to the rate law $-d[(C_6H_5)_3P]/dt = k_2[(C_6H_5)_3P][H_2NOSO_3^-]$. Second-order rate constants shown in Table III have been corrected for the small changes in $H_2NOSO_3^-$ concentration that occur during the runs. The average value of k_2 at 20.4° is 1.96 ± 0.10 M^{-1} sec^{-1}. At 12.4°, $k_2 = 1.40$ M^{-1} sec^{-1}, and at 29.7°, $k_2 = 3.12$ M^{-1} sec^{-1}, giving $\Delta H^\ddagger = 7.4 \pm 0.2$ kcal/mol and $\Delta S^\ddagger = -32 \pm 1$ eu. Variation of ionic strength in the range 0.002–0.10 *M* had no effect on k_2.

Table III. Kinetic Data for the Reaction of Triphenylphosphine with Hydroxylamine-*O*-sulfonate Ion at 20.4° in 50 wt % Methanol-Water[a]

$10^4[H_2NOSO_3^-]_0$, *M*	k_2, M^{-1} sec^{-1}	$10^4[H_2NOSO_3^-]_0$, *M*	k_2, M^{-1} sec^{-1}
5.00	2.07 (3)[b]	20.2	2.01 (2)
6.77	1.82 (3)	27.0	2.00
10.1	1.98 (7)	30.4	2.02
13.6	1.89 (4)	40.6	1.93

[a] $[(C_6H_5)_3P]_0 = (4.00\text{–}4.12) \times 10^{-5}$ *M*, [HOAc] = $[OAc^-]$ = 0.025–0.073 *M*, ionic strength = 0.065–0.10 *M*. [b] Number of runs.

Based on a potentiometric titration of 0.01 *M* H_3NOSO_3 in 50 wt % methanol-water, an approximate value at 20° of $K_a = 3 \times 10^{-3}$ was obtained for hydroxylamine-*O*-sulfonic acid. Since the pH of an equimolar acetate buffer in dilute 50 wt % methanol-water is 5.6,[26] H_3NOSO_3 is essentially completely converted (>99%) to the anion form under the reaction conditions. Values of k_2 were independent of hydrogen-ion concentration over a 25-fold range in various acetate buffers. At pH 8.15 in a phosphate buffer, $k_2 = 1.95$ M^{-1} sec^{-1}. Thus, the second-order rate constants correspond to the reaction of $H_2NOSO_3^-$ ion. Below pH 3.5, values of k_2 decreased and in 0.24 *M* $HClO_4$, a value of $k_2 = 0.2$ M^{-1} sec^{-1} was observed. In these acidic solutions, both triphenylphosphine and the hydroxylamine-*O*-sulfonate ion are extensively protonated. Air oxidation of the phosphine and the complexity of the system discouraged a detailed kinetic study.

A value of k_2 was determined in a deuterated solvent mixture in which $D_2NOSO_3^-$ is the species undergoing substitution. In 50 wt % CH_3OD-D_2O, free of aldehydes, a value of $k_2 = 1.28$ M^{-1} sec^{-1} was obtained, leading to a ratio of second-order rate constants for protio *vs.* deuterio solvents $k_H/k_D = 1.5 \pm 0.15$.

Triethylamine–Hydroxylamine-*O*-sulfonate Reaction. The stoichiometry of the reaction between triethylamine and hydroxylamine-*O*-sulfonate ion (eq 5) has been reported.[27]

$$(C_2H_5)_3N + H_2NOSO_3^- \rightarrow (C_2H_5)_3NNH_2^+ + SO_4^{2-} \tag{5}$$

The reaction was assumed to be first order in each reactant. Plots of ln $([H_2NOSO_3^-]/[(C_2H_5)_3N])$ *vs.* time were linear for the extent of reaction examined, *ca.* 2 half-lives, with either $H_2NOSO_3^-$ or $(C_2H_5)_3N$ in excess. Both $(C_2H_5)_3N$ and $(C_2H_5)_3NH^+$ were present under the reaction conditions, but only free amine reacted since addition of acid to completely protonate the amine stopped the reaction. Free triethylamine concentrations were calculated for each data point using $K_B = 1.0 \times 10^{-3}$ in water at 20° and 0.10 *M* ionic strength.[28] Values of k_2 were determined from a least-squares fit of the data to the equation $k_2 = (1/t)(B_0 - A_0)^{-1} \ln([B]A_0/[A]B_0)$, where B = $H_2NOSO_3^-$ and A = $(C_2H_5)_3N$. The rate constants are independent of $[OH^-]$,

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(20) The reported value 22.3 M^{-1} hr^{-1} was estimated to be 0.024 M^{-1} sec^{-1} at 20.4°, using $\Delta H^\ddagger = 11.6$ kcal/mol as a rough approximation. Extrapolation of the data in Table II to 0.1 *M* H^+, using eq 3, gave k_2(obsd) = 0.039 M^{-1} sec^{-1}.

(21) Oxidation of Br^- by H_3NOSO_3 is detectable but only at much higher concentrations than those in the present study. The reaction of coordinated $H_2NOSO_3^-$ in $Ir(NH_3)_5NH_2OSO_3^{2+}$ with Cl^- in 4.5 *M* H_2SO_4 has been reported for which $k_2 = 1.25 \times 10^{-3}$ M^{-1} sec^{-1}.[7]

(22) E. F. Caldin, "Fast Reactions in Solution," Wiley, New York, N. Y., 1964, p 244.

(23) This assumption was checked by measuring the ^1H nmr spectrum of a solution in 99.8% D_2O containing 0.5 *M* H_3NOSO_3 and 1.0 *M* $NaC_2H_3O_2$. No separate peak corresponding to nonexchanged protons in $H_2NOSO_3^-$ was observed and the residual H_2O peak was broadened, presumably due to rapid exchange with $H_2NOSO_3^-$.

(24) (a) H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Amer. Chem. Soc.*, 81, 2982 (1959); (b) S. R. Jain, W. S. Brey, Jr., and H. H. Sisler, *Inorg. Chem.*, 6, 515 (1967).

(25) $(C_6H_5)_3PO$ might also have been produced by attack of $(C_6H_5)_3P$ on the bridge oxygen in $H_2NOSO_3^-$.

(26) R. G. Bates, "Determination of pH," Wiley, New York, N. Y., 1964, p 226.

(27) (a) H. H. Sisler, R. A. Bafford, G. M. Omietanski, B. Rudner, and R. J. Drago, *J. Org. Chem.*, 24, 859 (1959); (b) R. Gosl and A. Meuwsen, *Chem. Ber.*, 92, 2521 (1959).

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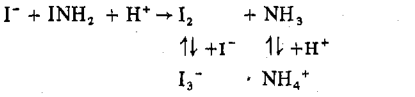
with an average value of $k_2 = 0.022 \pm 0.002\ M^{-1}\ \text{sec}^{-1}$ at 20.0° (Table IV).

***N*-Methylhydroxylamine-*O*-sulfonate.** The reaction of triphenylphosphine with $CH_3NHOSO_3^-$ was very slow. Because of concomitant hydrolysis of the $CH_3NHOSO_3^-$, a detailed study of the system was not feasible. Initial rates of disappearance of $(C_6H_5)_3P$ were measured at 290 nm (ϵ 3550). Assuming the reaction to be first order in each reactant, second-order rate constants were calculated for several initial concentrations (Table V). Over the small range of concentrations accessible, the data do conform to the assumed rate law with $k_2 = 1.7\ (\pm 0.2) \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$. Because $[CH_3NHOSO_3^-]_0 \gg [(C_6H_5)_3P]_0$, it is possible that an impurity in the $CH_3NH_2OSO_3$ may have affected the kinetics (although the major impurity expected, $CH_3NH_2OH^+$, had no affect on the reaction). Although the rate constant is regarded as approximate, it serves as an upper limit for the reaction. Iodide was also examined as a nucleophile, but the rate of formation of triiodide was extremely low. Based on initial rates, I^- is at least 10^4 less reactive toward $CH_3NHOSO_3^-$ than $H_2NOSO_3^-$.

Discussion

The mechanisms proposed are based on eq 1. A single bimolecular step, identical with the stoichiometry, is suggested for the reaction of triphenylphosphine (eq 4) and of triethylamine (eq 5). For the iodide reaction, with pH >3, reactions 6 and 7 are proposed, accompanied by a parallel

$$I^- + H_2NOSO_3^- \rightarrow INH_2 + SO_4^{2-} \text{ (rate determining)} \qquad (6)$$



$$\begin{array}{llll} I^- + INH_2 + H^+ \rightarrow & I_2 & + NH_3 & \\ & \uparrow\downarrow +I^- & \uparrow\downarrow +H^+ & \\ & I_3^- & NH_4^+ & \end{array} \qquad (7)$$

attack of I^- on H_3NOSO_3 in the pH region 1-3. The second-order rate laws and large, negative entropies of activation observed, in the case of $(C_6H_5)_3P$ and I^-, support the proposed mechanisms. A key feature of the mechanisms is attack by the nucleophile on the nitrogen atom. The identification of $(C_6H_5)_3PNH_2^+$ and $(C_2H_5)_3NNH_2^+$ [27] as principal products of the triphenylphosphine and triethylamine reactions, respectively, provides strong evidence for such attack on nitrogen. Because INH_2 is rapidly reduced by I^-, product evidence is not available for the iodide reaction. However, attack on the bridge oxygen as an alternative would require NH_2^- as the leaving group in the case of $H_2NOSO_3^-$, or NH_3 as the leaving group in the case of H_3NOSO_3. Oxygen attack can be ruled out since H_3NOSO_3 clearly should be the more reactive of the two forms, in contrast with the kinetic behavior observed.

The fact that a normal rather than an inverse isotope effect is observed for the $(C_6H_5)_3P$ reaction ($k_H/k_D = 1.5$) is consistent with the earlier conclusion that nitrogen attack takes place. By contrast, attack on oxygen, with either ND_2^- or ND_3 as the leaving group, is expected to give rise to a substantial inverse effect.[29] The value of $k_H/k_D = 1.3$ for I^- suggests that the iodide reaction involves attack on nitrogen, also.

For SN2 reactions at sp^3 carbon, deuterium isotope effects are usually close to unity.[30] The k_H/k_D values observed here represent a combination of an internal, secondary effect ($H_2NOSO_3^-$ *vs.* $D_2NOSO_3^-$) and an external solvation effect. These effects have been discussed in detail.[31] However, it is not possible to separate the two in the present study in which the solvent contribution, arising from interaction of D_2O (or CH_3OD) with the NH_2 group and the SO_4^{2-} leaving group, may be rather large.

Table IV. Kinetic Data for Reaction of Triethylamine with Hydroxylamine-*O*-sulfonate Ion at 20.0° and 0.100 *M* Ionic Strength

$[H_2NOSO_3^-]_0$, *M*	$\Sigma[(C_2H_5)_3N]_0$, *M*	$[(C_2H_5)_3N]_0$, *M*	$10^3[OH^-]_0$, *M*	k_2, M^{-1} sec^{-1}
0.0170	0.0389	0.0358	11.9	0.0214
0.0191	0.0357	0.0301	5.6	0.0218
0.0178	0.0268	0.0066	0.33	0.0232

Table V. Results of an Initial Rate Study of the *N*-Methylhydroxylamine-*O*-sulfonate–Triphenylphosphine Reaction at 20.4° in 50 wt % Methanol–Water[a]

$10^2[CH_3NHOSO_3^-]_0$, *M*	$10^4 \cdot [(C_6H_5)_3P]_0$, *M*	10^3k_2, M^{-1} sec^{-1}
0.91	2.40	1.8
1.00	2.40	1.5[b]
1.50	1.20	1.4[b]
1.50	2.40	1.6[b]
2.00	2.40	1.7[b]
2.30	2.40	1.7
3.00	1.20	2.0[b]
3.00	2.40	1.6

[a] Acetate buffer, pH 5.6, ionic strength 0.10 *M*. [b] Average of two or more runs.

The very low reactivity of $(C_6H_5)_3P$ and I^- toward $CH_3NHOSO_3^-$ observed here is in agreement with the results of Smith, *et al.*, who find that increasing alkyl replacement on H_3NOSO_3 greatly decreases reactivity toward iodide. The rate decrease that accompanies replacement of H by CH_3 on nitrogen has been ascribed to a large steric influence[6] and to electron donation by CH_3 groups.[32] Apparently, steric effects dominate when, as in the present study, SO_4^{2-} is the potential leaving group, since replacement of H by any of the electron-withdrawing groups, $C_6H_5C(O)$-,[33] C_6H_5-,[35] or O_3S-,[36] also results in very low reactivity toward iodide.

A significant result of the present study is the somewhat greater reactivity observed for $H_2NOSO_3^-$ than for the molecular form, which probably exists predominantly as H_3NOSO_3 and to a much lesser extent as H_2NOSO_3H.[37] H_3NOSO_3 might be expected to be more reactive than $H_2NOSO_3^-$ because of the resulting lower net charge on the activated complex and the greater susceptibility of the protonated nitrogen atom to nucleophilic attack.[6] However, some other factor must be involved to account for the lower reactivity of H_3NOSO_3. An appealing possibility is that

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(29) J. H. Krueger, *J. Amer. Chem. Soc.*, 91, 4974 (1969).

(30) (a) S. Seltzer and A. A. Zavitsas, *Can. J. Chem.*, 45, 2023 (1967); (b) K. T. Leffek and J. W. MacLean, *ibid.*, 43, 40 (1965).

(31) (a) E. K. Thornton and E. R. Thornton in "Isotope Effects in Chemical Reactions," ACS Monograph No. 167, C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N. Y., 1970, p 213; (b) E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 109 (1963).

(32) L. K. Krannich and H. H. Sisler, *Inorg. Chem.*, 11, 1226 (1972).

(33) Qualitative tests with the pyridinium salt of $C_6H_5CONHOSO_3^-$, prepared by the method of Daniher,[34] showed no detectable reactivity toward iodide.

(34) F. A. Daniher, *J. Org. Chem.*, 34, 2908 (1969).

(35) E. Boyland and R. Nery, *J. Chem. Soc.*, 5217 (1962).

(36) J. P. Candlin and R. G. Wilkins, *J. Chem. Soc.*, 3625 (1961).

(37) Although the molecular acid is generally assumed to be present as $H_3N^+OSO_3^-$ in water,[6,7] there is no experimental evidence that bears on the question of the site of protonation. The zwitterionic structure has been verified in the solid acid and its presence in dimethylformamide inferred from but not required by the single proton resonance observed in that solvent. R. E. Richards and R. W. Yorke, *J. Chem. Soc.*, 2821 (1959).

protonation of the nitrogen lone pair in H_3NOSO_3 eliminates the opportunity for stabilization in the transition state by π overlap between the lone pair and low-lying, unfilled orbitals on I^- or $(C_6H_5)_3P$. Thus, the lower reactivity of H_3NOSO_3 can be understood if this effect dominates over the charge effects.[38]

The observed order of nucleophilicity at trivalent nitrogen in $H_2NOSO_3^-$ is $(C_6H_5)_3P > I^- > (C_2H_5)_3N \gg Br^-, Cl^-$. It appears that polarizability and ease of oxidation of the nucleophile play a considerably more important role than does proton basicity in determining reactivity toward this trivalent nitrogen center. The appreciable nitrogen nucleophilicity of $(C_2H_5)_3N$ can be understood in terms of its softness and tendency for strong covalent interactions as a base.[39] Clearly, proton basicity is not an important factor, since OH^- shows little reactivity (pH 10-12) toward $H_2NOSO_3^-$.

Results for a wider range of nucleophiles are required before a detailed comparison of trivalent nitrogen with other acid centers is made. However, with respect to the order of nucleophilicity and possible π interaction of the nonbonded electron pair, there is a resemblance between trivalent nitrogen and Pt(II).

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Registry No. $(C_6H_5)_3PNH_2^+HSO_4^-$, 41380-11-4; $H_2NOSO_3^-$, 41380-12-5; I^-, 20461-54-5; $(C_6H_5)_3P$, 603-35-0; $(C_2H_5)_3N$, 121-44-8; $CH_3NHOSO_3^-$, 41380-13-6; hydroxylamine-*O*-sulfonic acid, 2950-43-8; *N*-methylhydroxylamine-*O*-sulfonic acid, 3400-11-1.

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[38] However, in a related system in which $H_2NOSO_3^-$ is coordinated to Ir^{III}, presumably through the nitrogen lone pair,[7,21] $H_2NOSO_3^-$ is subject to slow, but measurable attack by Cl^-, in contrast with the lack of reactivity between Cl^- and free H_3NOSO_3.

[39] R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, 93, 6014 (1971). In terms of C_B (covalent) and E_B (electrostatic) parameters, triethylamine possesses both a relatively large C_B value (inherent strength) and a high C_B/E_B ratio (softness).

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Preparation of Isopropyl and *tert*-Butyl Difluorophosphites

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tert-Butyl difluorophosphite and the previously reported isopropyl difluorophosphite have been prepared by the direct reaction of PF_3, pyridine, and the appropriate alcohol. PF_2O-*i*-Pr forms a stable adduct with borane but PF_2O-*t*-Bu appears to be reduced in the direct reaction with B_2H_6. Base displacement reactions have established the base strength toward borane as PF_2O-*i*-Pr > PF_2OEt > PF_2OMe. The basicity order is mirrored by the series of values for the J_{PB} coupling constants and the BH stretching frequencies.

The utility of the reaction of PF_3, pyridine, and alcohol for the production of difluorophosphites has recently been shown.[1,2] The preparation of PF_2O-*i*-Pr and PF_2O-*t*-Bu extends the generality of the reaction.

To examine the effect of the R (Me, Et, *i*-Pr, *t*-Bu) group[1] upon the basicity of these difluorophosphites toward borane, we have prepared PF_2O-*i*-Pr$\cdot BH_3$ and have attempted the preparation of PF_2O-*t*-Bu$\cdot BH_3$. The basicity order, as determined by displacement reactions,[1-5] is reported for the methyl, ethyl, and isopropyl derivatives.

Experimental Section

Material. Commercial PF_3 (Ozark-Mahoning), C_5H_5N, isopropyl alcohol and *tert*-butyl alcohol (Mallinckrodt), SbF_3 (Allied Chemical), B_2H_6 (Callery), and $(CH_3)_3SiCl$ (PCR) were used without further purification. Galvinoxyl[6] was prepared by literature methods.

General Techniques. Standard high-vacuum techniques were employed throughout.[7] Molecular weights were determined by *PVT* measurements and mass spectra recorded on a Varian M66 (70 eV). ^{19}F nmr spectra were obtained on a Varian T-60 and a Jeol JNM-C-60 HL operating at 56.4 MHz while proton nmr spectra were determined with a Jeol MN-100 operating at 100 MHz. ^{11}B spectra were recorded at 32.1 MHz on a Varian Associates XL-100 nmr spectrometer. Internal tetramethylsilane (except where noted) and external $CFCl_3$ and $B(C_2H_5)_3$ served as references for ^1H, ^{19}F, and ^{11}B spectra, respectively. Infrared spectra were recorded at a sample pressure of 10 mm on Perkin-Elmer 137 NaCl and 421 grating spectrophotometers using a 10-cm gas cell with KBr windows.

Synthesis of PF_2O-*i*-Pr and PF_2O-*t*-Bu. PF_2O-*i*-Pr[8] and PF_2O-*t*-Bu were prepared by the reaction of PF_3, pyridine, and the corresponding alcohol in a manner similar to the preparation of PF_2OCH_3, $PF_2OC_2H_5$, and $PF_2OCH_2CF_3$.[1,2] In the preparation of PF_2O-*t*-Bu, reaction time was 12 rather than 2.5 hr. The yields for the preparation of PF_2O-*i*-Pr and PF_2O-*t*-Bu were 50 and 25%, respectively.

The nmr spectra are consistent with the assigned structures. The ^1H spectrum of PF_2O-*t*-Bu (−40 to 0°, $CHCl_3$) consists of a singlet (δ_{CH_3} 1.49 ppm),[9] while the ^{19}F spectrum (−40°, $CHCl_3$) is a doublet (δ_F 41.3 ppm (d, J_{PF} = 1345 Hz)). These values are similar to those reported for other difluorophosphites.[10,11]

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