

amine, $\phi = 1.1$. In the polychromatic irradiation a larger proportion of the light is absorbed by the transient than in irradiation at 334 nm, near λ_{\max} of SBBS, and lower apparent quantum yields result. When the quantum yield at 334 nm in the presence of 0.030 *M* naphthalene, $\phi = 0.38$, is applied to the corresponding experiment of Table II and to the data at lower concentrations of quencher, extrapolation leads to a limiting $\phi = 2.2$. This is higher than the theoretical maximum, $\phi = 2.0$, and may reflect the errors in these experiments and in translating data obtained on the monochromator to those obtained with polychromatic light.

Photoreduction of SBBS by aqueous 2-propanol was also strongly retarded by a mercaptan, dimethylaminoethanethiol, DMAET, used as the hydrochloride at pH 5.75, Table IV. Although amines interact rapidly with ketone triplets,¹⁹ the unshared electrons of nitrogen appear to be required and the protonated amino group probably does not interfere. The retardation presumably arises from the previously described repeating sequence of hydrogen atom transfer reactions,³ reduction of the alcohol derived radical by mercaptan and oxidation of the ketone derived radical by thiyl radical, eq 7 and 8. Although the mechanism is quite different from



that of physical quenching of triplet, a not dissimilar kinetic expression may be derived.²³ A plot of inverse rate against concentration of mercaptan may be constructed, with slope = 2000 *M*⁻² hr, similar to that for naphthalene. The mercaptan keeps the concentration of alcohol derived radical low, the absorbing intermediate is not observed, and the plot is linear. The extrapolated rate in the absence of mercaptan is 0.083 *M* hr⁻¹, 1.7 times that of the standard, benzophenone-2-butylamine, corresponding to a hypothetical uninhibited quantum yield of ~ 1.9 . The quantum yield was also determined at 334 nm by ferrioxalate actinometry in the presence of 0.024 *M* DMAET, experiment 5, Table III, $\phi = 0.35$. When this value is applied to the data of Table IV, the corresponding rate, 0.016 *M* hr⁻¹, and the extrapolated rate, 0.083 *M* hr⁻¹, lead to a hypothetical quantum yield in the absence of mercaptan, $\phi = 1.8$. This high nearly maximum extrapolated value of quantum yield arises from absence of intermediate in the presence of mercaptan, and stands in contrast to the lower quantum yield, $\phi = 1.1$, actually observed in the absence of mercaptan.

(23) S. G. Cohen, D. A. Laufer, and W. V. Sherman, *J. Amer. Chem. Soc.*, 86, 3060 (1964).

Oxidation of 2-Methoxyethanol to Methoxyacetic Acid by Nitric Acid Solutions

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Abstract: The oxidation of 2-methoxyethanol by nitric acid in sulfuric acid solution was studied using 60-MHz nmr to follow the rate of disappearance of the alcohol. Nitric oxide evolution and N₂O₃ and HONO in solution were also monitored. An activation energy of 17.9 kcal/mol was obtained for the overall reaction in the temperature range 4–27°. The rate of disappearance of 2-methoxyethanol follows first-order kinetics well in the range of 20–80% conversion. A plot of the logarithm of the rate constants vs. the acidity function *H*₀ gives a unit slope. A deuterium isotope effect of 3.9 was observed and indicates the rate-determining step involves cleavage of the 1-C–H bond. A mechanism is proposed which involves nitrosonium ion (NO⁺) as the active oxidizing agent. A rapid equilibrium between 2-methoxyethanol and 2-methoxyethyl nitrite exists under our oxidation conditions. The oxidation of 2-methoxyethanol by nitrosonium fluoroborate was studied and provides additional support for the role assigned to nitrosonium ion.

Although nitric acid has often been used in the oxidation of alcohols to organic acids, only a few studies have been made to determine the oxidation path. Ogata and his coworkers¹ have studied separately the kinetics of nitric acid oxidation of benzyl alcohol to benzaldehyde (which proceeds in dilute HNO₃) and the oxidation of benzaldehyde to benzoic acid (which proceeds only under strongly acid conditions). Ogata and Sawaki^{1c} have suggested that the radical ion, HNO₂⁺, is the oxidizing agent in the oxidation of benzyl alcohol to benzaldehyde in aqueous dioxane. They postulated

an abstraction of a hydrogen atom by HNO₂⁺ followed by nitrite formation between the resulting organic radical and NO₂. The nitrite ester then could hydrolyze to the aldehyde. For the oxidation of benzaldehyde to benzoic acid in aqueous dioxane–H₂SO₄, Ogata, Tezuka, and Sawaki^{1b} proposed a mechanism involving a rate-determining hydrogen abstraction from both hydrated and free benzaldehyde by protonated nitrogen dioxide, followed by rapid hydrolysis of the so-formed benzoyl nitrites to benzoic acid. The oxidation of ethanol by aqueous nitric acid at 100–200° and 30–40 atm has been studied by Silakhtarian, Blumberg, Nonkov, and Emanuel.² They proposed a chain reaction involving

(2) N. T. Silakhtarian, E. A. Blumberg, U. D. Nonkov, and N. M. Emanuel, *Dokl. Akad. Nauk SSSR*, 184, 376 (1969).

(1) (a) Y. Ogata, Y. Sawaki, F. Matsunaga and H. Tezuka, *Tetrahedron*, 22, 2655 (1966); (b) Y. Ogata, H. Tezuka, and Y. Sawaki, *ibid.*, 23, 1007 (1967); (c) Y. Ogata and Y. Sawaki, *J. Amer. Chem. Soc.*, 88, 5832 (1966).

ion radicals or radicals, although they gave no specific reaction scheme. Levitt,³ in a review of organic oxidations in acidic solution, stated that H_2ONO_2^+ , NO_2^+ , or NO_2 were the most probable oxidizing species in nitric acid medium and that H_2ONO^+ , NO^+ , or NO were the most probable oxidizing species in nitrous acid medium.

We have studied the direct oxidation of 2-methoxyethanol to 2-methoxyacetic acid by nitric acid in strongly acidic water solution at temperatures from 4 to 27°. By using 60-MHz nmr we measured the disappearance of 2-methoxyethanol, the appearance of methoxyacetic acid, and the equilibrium concentration of 2-methoxyethyl nitrite. By using visible and ultraviolet spectroscopy we measured nitrogen trioxide (N_2O_3) and nitrite group (RONO) in solution. We also measured the evolved gases and identified them as being primarily nitric oxide (NO) and small amounts of nitrogen dioxide (NO_2) and nitrous oxide (N_2O). A kinetic deuterium isotope effect of 3.9 was observed. No methoxyacetaldehyde intermediate was observed. A rapid equilibrium between 2-methoxyethyl nitrite and 2-methoxyethanol was found. A reaction scheme involving nitrosonium ion (NO^+) as the oxidizing agent and consistent with our experimental data is proposed.

Experimental Section

2-Methoxyethanol. Commercial 2-methoxyethanol (Dowanol EM) which was over 99.5% pure by gas chromatographic analysis was distilled and the center cut was used for kinetic studies.

2-Methoxyethyl Nitrite. A mixture of *n*-pentane (50 ml) and 2-methoxyethanol (15 g) was cooled to -5° and a stream of $\text{NO} + \text{NO}_2$ (Matheson N_2O_3) was passed through the mixture until the solution became blue-green. Additional pentane (50 ml) was added and the solution was washed several times with water and dried over anhydrous CaSO_4 . The pentane was removed by distillation at atmospheric pressure and the residue was fractionated at reduced pressures. At no time was the temperature in the distillation pot allowed above 50°. The product was collected at 32° (75 Torr); ir (CS_2) 1662 cm^{-1} (*trans* $\nu(\text{NO})$), 1614 cm^{-1} (*cis* $\nu(\text{NO})$); nmr (CCl_4) δ 4.82 ppm (t, 2, CH_2ONO), 3.59 ppm (t, 2, CH_2OCH_3), 3.33 ppm (s, 3, CH_3O).

2-Methoxyethyl Nitrate. 2-Methoxyethyl nitrate was prepared by modifying the preparation⁴ for methyl nitrate. 2-Methoxyethyl nitrate separated from the reaction medium as an oil only after pouring the solution (0.4 mol scale in methoxyethanol) into 1 l. of an ice-water mixture. The oil was washed twice with saturated NaCl salt solution, once with saturated salt solution made basic with NaOH to pH 11, and washed twice more with the salt solution. The oil was dried over anhydrous CaSO_4 and filtered. About 6 g of a colorless liquid was obtained: ir (CS_2) 1640 cm^{-1} (antisym $\nu(\text{NO}_2)$), 1275 cm^{-1} (sym $\nu(\text{NO}_2)$); nmr (CCl_4) δ 4.55 ppm (t, 2, CH_2ONO_2), 3.61 ppm (t, 2, CH_2OCH_2), 3.35 ppm (s, 3, CH_3O).

Caution: This compound is shock sensitive.

2-Methoxyethanol-1,1- d_2 . A solution of 7.8 g (0.066 mol) of ethyl methoxyacetate in 7 ml of dry tetrahydrofuran was added in a 20-min period to a stirred mixture of 1.8 g (0.043 mol) of LiAlD_4 (98% D, Metal Hydrides, Inc.) in 30 ml of dry tetrahydrofuran. After 160 min of reflux the mixture was treated with 10 ml of 75% ethanol. The liquids and solid were heated in a distillation apparatus and the fraction boiling in the range of 100–135° was collected. This material was then purified by gas-liquid partition chromatography. A 155 \times 0.63 cm stainless steel column packed with Porapak Q was used at 200° and 60 cc/min He flow: nmr (CCl_4) δ 4.02 ppm (s, 1, OH), 3.40 ppm (s, 2, CH_3OCH_2), 3.27 ppm (s, 3, CH_3O); mass spectrum, molecular ion *m/e* 78.

Oxidation Runs (Gas Measurements). A 100-ml, round-bottomed flask was fitted to a 100-ml gas measuring buret. The flask was fitted with a short 6 mm i.d. glass tube which angled up-

ward 45° from the base of the neck of the flask. A serum bottle stopper was attached to this arm so that reagents could be injected into the closed system with a hypodermic syringe. The flask was jacketed with a 250-ml flask which had inlet and outlet tubes for circulating water from a temperature-controlled bath. The fluid in the gas buret was of a low viscosity, low vapor pressure, and chemically inert, fluorinated aliphatic material (Fluorolube FS-5 from the Hooker Chemical Co.)⁵ After equilibrating the liquid in the buret with the gas to be measured, no gas volume change was observed. Appropriate quantities of water, sulfuric acid, and nitric acid were placed in the reactor which was then connected to the system. The solution was stirred with a magnetic stirring bar and after the control temperature was reached the alcohol was injected into the solution through the septum. Gas uptake and evolution were both recorded at short intervals. Gas samples were analyzed by glc with a 100 cm \times 0.63 cm SS column packed with molecular sieve type 5A, 70–80 mesh. With a program of 2 min initial temperature at 150° followed by a 60°/min rate to 400° and holding the controls at that position until all gases came through we were able to resolve O_2 (1.6 min), N_2 (1.8 min), NO (2.1 min), N_2O (7.1 min), and CO_2 (7.9 min). NO_2 could not be chromatographed. Helium flow rate was 50 cc/min at 60 psig. In a typical run at 25.0° no CO_2 was observed. The N_2O level was about 0.1–0.2 mol %. Small amounts of NO_2 (2 mol % or less) were observed by mass spectrometry. The primary reduced gas was NO . The volume of NO obtained after 275 min (*ca.* 85% complete) was 11.0 mmol from 10.2 mmol of alcohol. This volume corresponds to about 3.8 mol of $\text{NO}/3$ mol of $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ oxidized to $\text{CH}_3\text{OCH}_2\text{CO}_2\text{H}$. The yields of methoxyacetic acid, as determined by titration and glc analysis, were 95% or better when the reactions were allowed to go to completion.

Visible and Ultraviolet Spectrophotometry. In the visible region, the absorption of N_2O_3 at 635 $m\mu$ was monitored in a 1-cm path length cell. In the ultraviolet region, the absorption of RONO at 354 $m\mu$ was measured in a 0.1 mm cell and the region between 300 and 400 $m\mu$ was scanned at timed intervals before each measurement to establish the base line which was continuously increasing. During both of these experiments, erratic absorption data were obtained during the period of maximum rate due to bubbles formed in the solutions. Additional difficulty was encountered with measurement of RONO absorption because this absorption maximum was on the slope of the strong absorption maximum of N_2O_3 farther in the ultraviolet region.⁶

A Beckman DK-2 spectrophotometer was used for transmission measurements for N_2O_3 at 635 $m\mu$ and a Cary Model 11 spectrophotometer was used for absorption measurements of N_2O_3 and RONO. The sample chamber was continuously swept with nitrogen in both measurements. The solutions were prepared in volumetric flasks and the ambient temperature of the cell chamber was monitored. The temperature remained at $26 \pm 1^\circ$. See Figure 1 for the results.

Kinetic Runs. The rate data for the oxidation of 2-methoxyethanol to methoxyacetic acid were obtained by monitoring the disappearance of the C-2 nmr proton signals (as integrals of the signal) of 2-methoxyethanol, protonated 2-methoxyethanol, and 2-methoxyethyl nitrite at 60 MHz. The combined integrals of the signals of the methoxy protons of 2-methoxyethanol and methoxyacetic acid were used as references for changes in instrument behavior during a run. When no instrument changes occurred, the average of the integrals obtained during one-sixth to one-fourth experimental time intervals remained constant throughout the run. The values of the integrals obtained during successive scans varied, so many scans (80–110) were made during a run. The integrals were converted to concentrations, and the data were plotted and intercepts determined by computer. The data used to calculate the rates were those obtained after the induction period of the reactions. Usually two half-lives were monitored but in some instances data from one half-life were obtained.

Alcohol-Nitrite Ester Equilibrium. The 2-methoxyethanol-2-methoxyethyl nitrite ester equilibrium was monitored by the measurement of the C-1 proton signals relative to the OCH_3 resonance. Under the conditions studied here, the rate of exchange of OH protons with the NO group in the nitrite ester is fast so that only one set of absorptions is observed for the C-1 protons. The observed shift represents an average and depends on the chemical shifts of the alcohol and nitrite ester and on their concentration.⁷

(3) L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955).

(4) A. H. Blatt, Ed., "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 412.

(5) We are grateful to The Hooker Chemical Co. for a free sample.

(6) J. Mason, *J. Chem. Soc.*, 1288 (1959).

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolu-

This known dependence was used to calculate the nitrite ester concentration from the observed shifts.⁸ A plot of the relative nitrite ester concentration as a function of time is illustrated in Figure 1.

Reaction between 2-Methoxyethanol and NO^+BF_4^- . A solution of 2 ml of dry CH_3CN and 1.123 g of NO^+BF_4^- (95% NO^+BF_4^- ; used as received from Alfa Inorganics) was treated with 2.0 ml of 2.00 M 2-methoxyethanol in dry CH_3CN . After 1 min vigorous gas evolution took place. A sample of the gas was collected and analyzed by infrared spectrophotometry: N_2O , 1.8%; NO_2 <1%; CH_3CN , 14%; CH_3ONO , trace; NO , remainder.

In another experiment, 0.14 g of 2-methoxyethanol was treated with 0.441 g of NO^+BF_4^- in 1.5 ml of CD_3CN . After 22 min the mixture was examined by nmr. The spectrum of the solution indicated that a mixture of 2-methoxyethanol, 2-methoxyethyl methoxyacetate, methyl methoxyacetate, and methoxyacetic acid as well as other substances were present.

A third experiment, in which 0.096 g (1.26 mmol) of 2-methoxyethanol and 0.579 g (4.71 mmol) of NO^+BF_4^- were treated in 1.0 ml of dry CH_3CN for 12 min, was examined by gas-liquid chromatography and gas-liquid chromatography-time of flight mass spectrometry. Compared with the mass spectra of the known standards, the spectra of the separated components of the mixture were consistent with 2-methoxyethanol, methyl methoxyacetate, 2-methoxyethyl acetate, and 2-methoxyethyl methoxyacetate. By gas-liquid chromatography, the retention times of the components of the reaction mixture were the same as the standards with which each was identified. From the area of each peak the relative percentage of each component was estimated: 2-methoxyethanol, 2%; methyl methoxyacetate, 0.1%; 2-methoxyethyl acetate, 25%; methoxyacetic acid, 1%; 2-methoxyethyl methoxyacetate, 70%; and two unknown substances, 0.1 and 2%.

H_R Measurements. The acidities, H_R , of nitric acid and sulfuric acid mixtures were determined spectrophotometrically using 4-methyltriphenylmethanol as the indicator.⁹ Each acid mixture was prepared in duplicate in 50-ml volumetric flasks. To one solution of each pair was added 1.00 ml of 4.06×10^{-5} M 4-methyltriphenylmethanol in acetic acid. The second solution of each pair was used to establish the base line. The absorbance at 450 μm was measured in a 10-cm cell with the Model 11 Cary spectrophotometer. The absorbance at 450 μm of 1.00 ml of the indicator solution in 50 ml (total volume) of 70% H_2SO_4 was used as 100% carbonium ion concentration. The acidity¹⁰ obtained for 4.97 M H_2SO_4 + 2.66 M HNO_3 was -6.57; for 4.27 M H_2SO_4 + 2.66 M HNO_3 , H_R was -5.90; for 3.53 M H_2SO_4 + 2.66 M HNO_3 , H_R was -5.20.

Results

In agreement with the findings of other workers^{1,2} studying nitric acid oxidations, we found the oxidation of methoxyethanol has a marked induction period. During this period we found that N_2O_3 , HNO_2 , and 2-methoxyethyl nitrite form and increase in concentration until maximum levels are reached. These concentrations then decrease as the reaction proceeds. Figure 1

tion Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 221.

(8) Knowledge of the actual nitrite ester concentration was not necessary for purposes of illustrating the nitrite ester-alcohol equilibrium. The calculation of the actual concentration requires knowledge of the separate chemical shifts for the alcohol and ester under nonexchanging conditions. The alcohol shift in acid solution (1.3 M HNO_3 and 7.2 M H_2SO_4) was 21 Hz downfield for the OCH_3 reference. The shift for the nitrite ester under the same conditions could not be measured due to the rapid ester-alcohol exchange. An estimate of 88 Hz downfield relative to OCH_3 was obtained for the C-1 protons in the nitrite ester in acid solution. This value was obtained by comparison of shifts for the nitrate ester (which does not exchange rapidly with alcohol) in acid and in CCl_4 solutions with nitrite ester in CCl_4 . These values were used to estimate the concentration of nitrite ester formed during a typical run. The maximum value of nitrite ester found is about 0.25 M.

(9) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3044 (1955).

(10) The experimentally determined values of H_R for the nitric acid-sulfuric acid mixtures appear to be the sum of the H_R values for the corresponding nitric acid solutions and sulfuric acid solutions determined by Deno, *et al.*^{9,11}

(11) N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Peterson, *J. Amer. Chem. Soc.*, **81**, 2344 (1959).

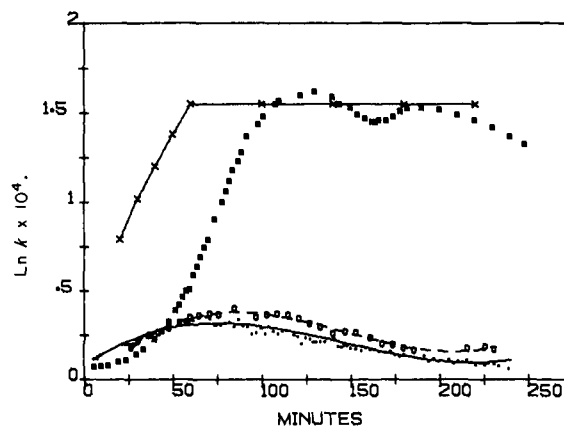


Figure 1. Composite plot of three reactions under the conditions 1.0 M $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, 2.7 M HNO_3 , 9.9 N H_2SO_4 at 27°. (a) \times , $\ln k$ vs. time demonstrates change in rate of reaction during induction period, read ordinate as $\ln k \times 10^4$; (b) \blacksquare , absorption of N_2O_3 at 635 μm in a 1 cm cell; dip in curve occurred during period of maximum gas evolution; read ordinate as absorbance; (c) \square , absorption of RONO at 354 μm in a 0.1 mm cell; read ordinate as absorbance; (d) \bullet , methoxyethyl nitrite concentration; read ordinate as millimoles per liter; these latter data and the kinetic data above were obtained from the same experiment.

illustrates the above observations. Gas evolution commences in about 15 min and increases in rate to a maximum and then gradually decreases. The induction period varied in time depending on the amount of initiator added to the system.¹² We used NO as the initiator. In the absence of NO , a solution consisting of 1.014 M 2-methoxyethanol, 7.15 M H_2SO_4 and 1.32 M HNO_3 showed no evidence of reaction after 277 min at 27° when examined by 60-MHz nmr. Another solution consisting of 0.40 M 2-methoxyethanol, 7.20 M H_2SO_4 , and 0.63 M HNO_3 showed no decrease in transmission at 640 μm (N_2O_3 absorption) after 18 hr at 25–28°. This same solution, when inoculated with a few cubic centimeters of NO , started to evolve gas within 18 min, and the N_2O_3 concentration increased to a maximum in 58 min as evidenced by the decrease in transmission at 640 μm from 93 to 13% in a 1-cm path length cell. The induction period can be reduced to a few minutes by holding an atmosphere of NO above the stirred reaction solution.

The amount of NO that the acid solution absorbed was measured with a gas buret. A solution consisting of 7.16 M H_2SO_4 and 0.604 M HNO_3 absorbed 0.17 mmol of NO at 25.0° in a 22-min period. At this point the rate of absorption was very slow. The characteristic intense blue color of N_2O_3 was present. Sufficient 2-methoxyethanol to make a 0.39 M solution was injected into the solution; the blue color lightened considerably. Within the next 5 min there was an additional rapid uptake of 0.065 mmol of NO . The intense blue color returned, then gas evolution commenced and continued for the remainder of the reaction.

Under controlled reaction conditions of 25° or less, the evolved gas was primarily NO . About 0.2% or less N_2O formed and NO_2 evolved was 2% or less. Under uncontrolled conditions where the temperature was allowed to rise to about 75° and the gas evolution

(12) The induction period also increased in time as the rate of oxidation decreased. For the maximum rates measured the induction period was around 45–60 min; for the slowest rates the induction period was around 120–150 min.

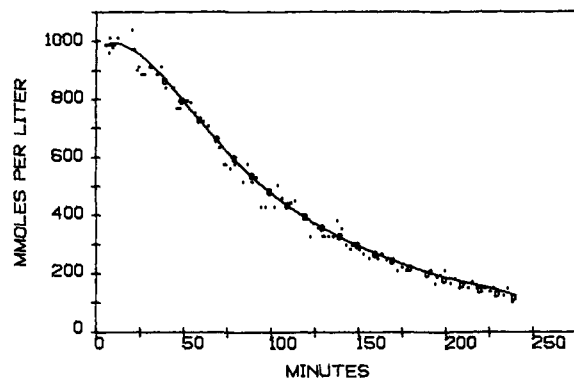
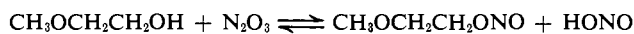
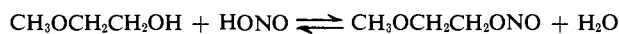


Figure 2. S-shaped curve obtained in a typical experiment: 4.97 M H_2SO_4 , 2.66 M HNO_3 , 1.007 M $CH_3OCH_2CH_2OH$, 27.0°.

was very vigorous, the gas composition changed to about 58% NO , 36% NO_2 , 2% CO_2 , and 3% H_2O . Again, N_2O formation was very low.

The existence of the rapid equilibration between 2-methoxyethanol and 2-methoxyethyl nitrite ester was established by a number of experiments. First, the downfield shift of the C-1 $-CH_2$ resonance signal as the



reaction proceeded indicated that a rapid equilibration was occurring between 2-methoxyethanol and a 2-methoxyethyl alcohol derivative. That this derivative was not a sulfate or methoxyacetate was established by placing 0.5 M methoxyethanol and 0.5 methoxyacetic acid together and 1.0 M methoxyethanol alone in 6.5 M H_2SO_4 . The downfield nmr shift (20.8 Hz) for the low frequency C-1 proton resonance peak, measured from the $-OCH_3$ peak, was the same in each case. With 2-methoxyethyl nitrate, in 4.32 M H_2SO_4 and 2.66 M HNO_3 , the low frequency C-1 proton signal (73 Hz downfield from $-OCH_3$) remains unchanged as its concentration changes with time. Therefore, the nitrate ester of 2-methoxyethanol is not responsible for the observed shift. The rapid disappearance of the blue color on addition of 2-methoxyethanol to the solution, the ease with which 2-methoxyethyl nitrite is formed from N_2O_3 , and the correspondence of the amount of shift to the concentration of N_2O_3 and HONO (Figure 1) suggest that this shift is due to rapid nitrite ester-alcohol equilibration. When methoxyethyl nitrite was added to 5.7 M H_2SO_4 the C-1 proton resonance shifted upfield as the concentration decreased and signals corresponding to methoxyacetic acid appeared. This indicates that as the nitrous acid is depleted by the oxidation process, the equilibrium shifts toward a greater fraction of 2-methoxyethanol.

The kinetic results are given in Table I. The rate data fit a first-order disappearance of C-2 proton nmr resonance signal from 20 to 80% conversion. This signal is a composite of 2-methoxyethanol, protonated 2-methoxyethanol, and 2-methoxyethyl nitrite. The beginning and end of the oxidation curve flattened to give an overall S-shaped curve such as that shown in Figure 2.

The rate constants based on the appearance of methoxyacetic acid were determined in two of the experiments. Values obtained were $1.9 \times 10^{-4} \text{ sec}^{-1}$

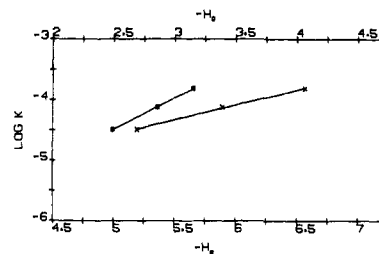


Figure 3. Plot of the log of the rate constants against $-H_R$ and $-H_0$: \times , read vs. $-H_R$; \square , read vs. $-H_0$.

(compared with $1.55 \times 10^{-4} \text{ sec}^{-1}$ for alcohol disappearance) and $1.7 \times 10^{-4} \text{ sec}^{-1}$ (compared with $1.33 \times 10^{-4} \text{ sec}^{-1}$). These values are considered less reliable since much of the data could not be used because the C-1 proton signal of the alcohol-nitrite ester equilibrium shifted across the singlet C-2 proton signal of methoxyacetic acid as the oxidation progressed.

Table I. Oxidation of 2-Methoxyethanol by Nitric Acid. Kinetic Results

$$\frac{d[\text{alc}]^a}{dt} = -k[\text{alc}]$$

—Init concn, M —			Temp, °C	$k \times 10^4$, sec^{-1}
$CH_3OCH_2CH_2OH$	HNO_3	H_2SO_4		
1.016	1.33	5.76	27.0	1.37
1.026	1.32	5.67	27.0	1.33
1.007	2.66	4.97	27.0	1.55
1.012	2.67	4.27	27.0	0.756
1.011	2.68	3.53	27.0	0.324
1.010	2.67	4.97	22.0	1.02
1.013	2.66	4.97	15.0	0.447
1.017	2.66	4.98	10.0	0.265
1.010	2.67	4.98	4.0	0.133
0.9795 ^b	2.66	4.97	27.0	0.394

^a $d[\text{alc}]$ here means the disappearance of the C-2 proton resonance signal due to methoxyethanol, methoxyethyl nitrite, and protonated methoxyethanol. ^b $CH_3OCH_2CD_2OH$.

The Arrhenius plot of the kinetic data gives a straight line with a slope which corresponds to an activation energy of 17.9 kcal/mol. The enthalpy of activation and entropy of activation calculated from this value correspond to 17.3 kcal/mol and -18.4 eu , respectively. The deuterium isotope effect (k_H/k_D) was found to be 3.93.

In three of the kinetic runs at 27° (Table I), the concentration of nitric acid was held constant and the concentration of sulfuric acid was varied. For these three acid concentrations, the acidity H_R was determined using *p*-methyltriphenylmethanol indicator as described by Deno, Jaruzelski, and Schriesheim.⁹ As shown in Figure 3, the plot of $\log k$ vs. $-H_R$ gives a slope of 0.5. Since the H_R values of H_2SO_4 and HNO_3 solutions separately determined and then added gave H_R values which closely approximated the H_R values determined experimentally for the mixtures, a similar behavior for H_0 for these acids in the region we were working was assumed. Using the literature values of H_0 for nitric acid and sulfuric acid,¹³ the plot of $\log k$ vs. $-H_0$ results in a slope of 1.

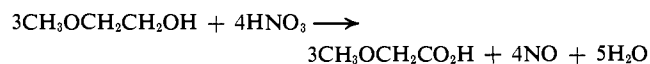
(13) M. A. Paul and F. A. Long, *Chem. Rev.*, 57, 1 (1957).

The reaction of 2-methoxyethyl nitrate in an oxidizing medium was slow. Under conditions equivalent to 7.5 half-lives for oxidation of methoxyethanol, 71% of the nitrate ester was still unreacted. The solution contained 19 mol % methoxyacetic acid and 10 mol % of the equilibrium mixture 2-methoxyethanol and methoxyethyl nitrite.

The presence of methoxyacetaldehyde of NO_2 could not be detected with nmr under our conditions although NO_2 gas in about 2% concentration is present above the solution. The initial green solution obtained when the $\text{HNO}_3\text{-H}_2\text{SO}_4$ solution is treated with NO turns to a deep blue solution after the reaction proceeds. No disturbance of the nmr resonance signals due to the odd electron of NO_2 is observed while the reaction is in progress. This suggests that less than $10^{-3} M \text{NO}_2$ is present; at this level some broadening of signals is expected. Signal broadening was observed with a solution of methoxyacetic acid in nitric acid which was green in color. In the ultraviolet, the region of absorption maximum for NO_2 around $405 \text{ m}\mu^{14}$ was partially obscured by the tail of the strong absorption of N_2O_3 farther in the ultraviolet region. No shoulder or superimposed absorption could be observed in this region with 0.1 mm or 10 mm path length cells during an oxidation run.

Discussion

Since NO is the dominant reduced product and methoxyacetic acid is the only observed oxidized product, the stoichiometry for the reaction is



The amount of NO obtained in this reaction approached that expected by the above equation. The high yields (95–98%) of methoxyacetic acid obtained in these studies argue against free-radical intermediates because other products resulting from hydrogen abstraction, dissociation, disproportionation, or coupling, all indicative of radical reactions, are not formed. Methoxyacetaldehyde, expected as an intermediate, was not observed by nmr at any time in any of the reactions. If methoxyacetaldehyde is formed, it is oxidized much faster than methoxyethanol under our highly acidic reaction conditions, and its concentration never builds up to an amount (1%) sufficient for detection.¹⁵ Although the presence of NO_2 could not be detected by nmr in the reaction medium, a small amount (2% yield) was detected by mass spectrometry in the evolved gases. The production of NO_2 in the gas phase can be explained by the reaction of nitric acid with NO



($P^3_{\text{NO}_2}/P_{\text{NO}} = 3.64 \times 10^{-5} \text{ atm}^2$),¹⁶ and/or by the dissociation of N_2O_3



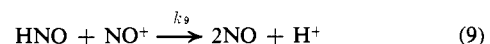
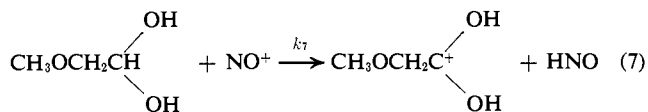
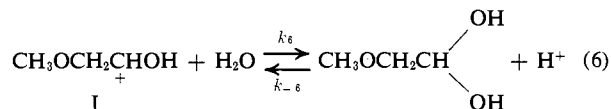
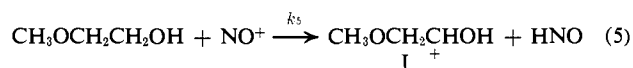
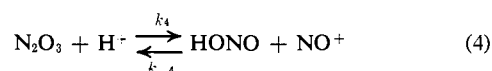
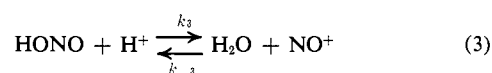
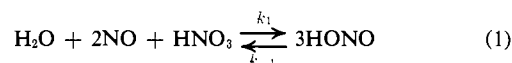
(14) T. C. Hall and F. E. Blacet, *J. Chem. Phys.*, **20**, 1745 (1952).

(15) Interestingly, in a run at 2.2 M H_2SO_4 with ethanol instead of methoxyethanol, the presence of acetaldehyde could be observed. Its concentration gradually reached a maximum and then dropped to zero as the oxidation proceeded. It should be noted that at this lower acidity, the oxidation is occurring in an acidity range intermediate between that (<1.5 M acid) in which the oxidation stops at the aldehyde stage^{1a} and that (4–5 M acid) in which organic acid is the only observable product.

(16) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1944, p 79.

Trace amounts of N_2O were also detected in the gas phase.

As the S-shaped reaction curve (Figure 2) suggests, the reaction is autocatalytic;¹⁷ NO, the end reduced product, is required in the sequence of reactions which involves the production of nitrosonium ion (NO^+) which we propose is the oxidizing agent. In the absence of NO or NO-producing agents, no reaction takes place. The induction period increases as the rate of the reaction is decreased by (1) lowering the temperature or (2) lowering the acid concentration or (3) replacing hydrogen with deuterium on C-1. This behavior is expected in autocatalytic reactions since a longer time is required to reach higher concentrations of the critical agent in the oxidation step. Taking into account the above facts and those already in the literature for equilibria between HNO_3 and various oxides of nitrogen, the reaction scheme given in eq 1–9 is proposed for the nitric acid oxidation of methoxyethanol to methoxyacetic acid. (It is understood that both H^+ and NO^+



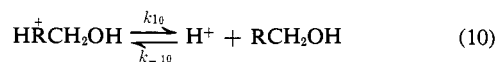
are solvated.) Since a C-1 deuterium isotope effect of 3.9 is observed, eq 5 is considered to be the rate-determining step. Of the three species, 1-methoxyethanol, protonated 1-methoxyethanol, and 1-methoxyethyl nitrite, methoxyethanol is probably being oxidized at the fastest rate. The protonated alcohol, bearing a positive charge, is not likely to be approached by the positively charged nitrosonium ion. Protonation at the ether linkage also would be expected to slow down the oxidation at the C-1 carbon relative to the oxidation of the free alcohol. The nitrite group of methoxyethyl nitrite would be expected to have an electron-withdrawing effect similar to the nitrate group of methoxyethyl nitrate which oxidizes very slowly compared to the methoxyethanol mixture. The rate expression, based on

(17) W. E. Wallis and T. E. Platt, *Ind. Eng. Chem.*, **59** (6), 41 (1967).

the disappearance of the C-2 proton resonance signals, then becomes

$$\frac{-d([\text{RCH}_2\text{OH}] + [\text{HR}^+\text{CH}_2\text{OH}] + [\text{RCH}_2\text{ONO}])}{dt} = k_5[\text{RCH}_2\text{OH}][\text{NO}^+]$$

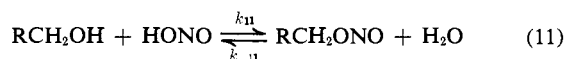
where $\text{R} = \text{CH}_3\text{OCH}_2-$. From equilibrium equations the terms within the parentheses can be expressed as functions of methoxyethanol, nitric acid, water, and acidity. From the equilibrium reaction



protonated methoxyethanol can be expressed as

$$[\text{HR}^+\text{CH}_2\text{OH}] = \frac{[\text{RCH}_2\text{OH}]h_0}{K_{10}}$$

and from the equilibrium reaction



methoxyethyl nitrite can be expressed as

$$[\text{RCH}_2\text{ONO}] = K_1'K_{11} \frac{[\text{RCH}_2\text{OH}][\text{HNO}_3]^{1/2}}{[\text{H}_2\text{O}]^{2/3}}$$

where

$$K_1' = \frac{[\text{HONO}]}{[\text{HNO}_3]^{1/2}[\text{H}_2\text{O}]^{1/2}}$$

Since NO gas is evolved during oxidation at constant partial pressure, the NO concentration in solution is considered at saturation and constant and is incorporated into K_1 as K_1' .

The nitrosonium ion concentration can also be expressed in terms of nitric acid, water, and acidity

$$[\text{NO}^+] = \frac{K_3K_1'[\text{HNO}_3]^{1/2}h_R}{[\text{H}_2\text{O}]^{2/3}}$$

By these substitutions the rate expression becomes

$$\frac{-d[\text{RCH}_2\text{OH}]\left\{1 + \frac{h_0}{K_{10}} + \frac{K_1'K_{11}[\text{HNO}_3]^{1/2}}{[\text{H}_2\text{O}]^{2/3}}\right\}}{dt} = \frac{k_5K_1'K_3[\text{RCH}_2\text{OH}][\text{HNO}_3]^{1/2}h_R}{[\text{H}_2\text{O}]^{2/3}}$$

For a 100% reaction 1.67 mol of water is produced/mole of alcohol oxidized. The initial water concentrations in these studies are in the range of 30–35 *M* and for a 1.0 *M* alcohol run the expression $[\text{H}_2\text{O}]^{2/3}$ will increase to a maximum of 3% over the initial concentration so the water concentration can be considered constant. The initial nitric acid concentration is 2.67 *M* and at the completion of the reaction the concentration would be 1.33 *M*. The third root of these values are 1.39 and 1.10, respectively. During the 20–80% part of the reaction, where the nitric acid concentration changes even less, the expression $[\text{HNO}_3]^{1/2}$ would be expected to change much less than 21% so that, as a first approximation, it is considered as constant. The rate expression then becomes

$$\frac{-d[\text{RCH}_2\text{OH}]}{dt} = k_{\text{obsd}}[\text{RCH}_2\text{OH}]h_R$$

where

$$k_{\text{obsd}} = \frac{k_5K_1'K_3}{\frac{(\text{H}_2\text{O})^{2/3}}{(\text{HNO}_3)^{1/2}}\left(1 + \frac{h_0}{K_{10}}\right) + K_1'K_{11}} \quad (12)$$

On integration this becomes

$$\ln [\text{RCH}_2\text{OH}] = k_{\text{obsd}}h_R t + c$$

Plotting the logarithm of the rate constant against an acidity function should give a unit slope. This occurs when the acidity function H_0 is used.

A unit slope relationship was observed between $-H_R$ and log of the rate constant in the oxidation of formic acid (slope 0.93–1.12),^{9,18} and in the diazotization of benzamide by nitrous acid in concentrated sulfuric acid (slope 0.96).¹⁹ In both cases prior ionization of nitrous acid to nitrosonium ion was indicated.

In our work, the basicity of 2-methoxyethanol and possibly the presence of N_2O_3 can cause the plot of log k_{obsd} vs. $-H_R$ to deviate from unit slope. Our plot of log k_{obsd} vs. $-H_R$ results in a slope of 0.5. We attempted to establish the basicity of 2-methoxyethanol by use of nmr and laser Raman spectroscopy but we were unsuccessful. The total solubility of 2-methoxyethanol in water does not make possible the solvent extraction–glc technique²⁰ for determination of basicities of weak bases. We then used as an approximation the value of -2.4 for pK_{10} . This value was obtained from the H_0 for half-ionization for *n*-butyl alcohol found by Arnett and Anderson.²¹ Since our work covers the short range of 2 H_0 units we made the further assumption that the basicity follows Hammett's acidity function with unit slope. Numerical values were calculated for the denominator in expression 12 for each of the three experiments in which the acid concentrations were varied and then the values of k_{obsd} were changed to keep the denominator value constant. The log of this corrected k_{obsd} (see Table II) was then plotted against $-H_R$

Table II. Corrected k_{obsd} Relative to k_{obsd} at $H_0 = -2.50$ (3.53 *M* H_2SO_4 + 2.66 *M* HNO_3), $\text{HNO}_3 = 2.67 \pm 0.01$ *M*, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH} = 1.0$ *M*, $t = 27^\circ$, $p = 1$ atm

$[\text{H}_2\text{SO}_4]$, <i>M</i>	h_0/K_{10}	Denominator, ^a $\text{mol}^{1/3}$	Log corr $k_{\text{obsd}} \times 10^4$ sec^{-1}
4.97	1.25	50.7	-3.57
4.27	2.95	64.8	-4.02
3.53	5.75	88.0	-4.49

^a The figures used to calculate the numerical values for the denominator of expression 12, $\{(\text{H}_2\text{O})^{2/3}/(\text{HNO}_3)^{1/2}[1 + (h_0/K_{10}) + K_1'K_{11}]\}$, were $(\text{H}_2\text{O})^{2/3}/(\text{HNO}_3)^{1/2} \sim 8.23$ $\text{mol}^{1/3}$, $K_1' = 0.32$ $\text{mol}^{1/3}$ at 1 atm NO ,¹⁶ $K_{11} \sim 100$ which was calculated from the concentrations of HNO_2 , $\text{CH}_3\text{OCH}_2\text{CH}_2\text{ONO}$, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ observed, and H_2O calculated at different times during a run.

and a straight line which had a slope of 0.67 was obtained. A pK_{10} value of -1.8 for 2-methoxyethanol would result in a slope of 1 for a plot of log k_{obsd} corrected vs. $-H_R$. The value of $pK_{10} = -1.8$ is not un-

(18) J. V. L. Longstaff and K. Singer, *J. Chem. Soc.*, 2604, 2610 (1954).

(19) H. Ladenheim and M. L. Bender, *J. Amer. Chem. Soc.*, **82**, 1895 (1960).

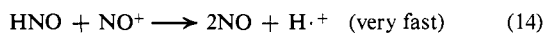
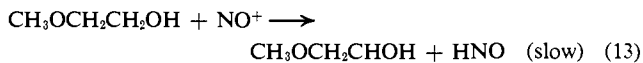
(20) E. M. Arnett, C. Y. Wu, J. N. Anderson, and R. D. Bushick, *ibid.*, **84**, 1674, 1680, 1684 (1962).

(21) E. M. Arnett and J. N. Anderson, *ibid.*, **85**, 1542 (1963).

reasonable for 2-methoxyethanol with its two oxygen atoms which are positioned in such a manner that a five-membered ring chelate with a proton could occur. The conclusion is made that there is a good possibility that the basicity of 2-methoxyethanol is significant enough to affect the slope of these plottings.

A further complication is the presence of N_2O_3 (estimated to be 0.08 *M* at maximum concentration in the run which had 4.97 *M* H_2SO_4 and 2.66 *M* HNO_3 initial concentrations)²² in our experiments. The N_2O_3 may act as a dehydrating or buffering agent on the water concentration so that the acidity function, H_R , is affected.

The concentration of NO^+ is dependent on the concentrations of HNO_2 and the presence of other strong acids. The equilibrium between HNO_2 and NO^+ has been studied in H_2SO_4 solutions by a number of investigators.^{18,23} Bayliss^{23a} found that between 5.6 and 11.5 *M* H_2SO_4 the mole fraction of NO^+ increased from 0 to 1.00 at 4.5° and relationships between acidity functions and degree of NO^+ formation were obtained. Our system contains both HNO_3 and H_2SO_4 . The system is further complicated by the equilibria in which HNO_3 is involved. Based on the results of Bayliss, we estimate that the mole fraction of NO^+ present is 0.02 or less at the highest rate studied by us and drops to lower values as the H_2SO_4 concentration is lowered. Since the maximum $HONO$ concentration is about 0.5 *M*,²⁴ the maximum NO^+ concentration is about 0.01 *M*. From the data given by Bayliss^{23a} on the appearance of nitrosonium ion with increasing acidity, it is evident that in the range of acidity used in our study, the concentration of nitrosonium ion is just beginning to build up. At higher acidities, nitrous acid is converted largely to nitrosonium ion, and at these higher acidities, the oxidation of 2-methoxyethanol proceeds violently. The role of NO^+ as an oxidizing agent fits the pattern of preferred two-electron oxidation step of an organic molecule (13) followed by one-electron exchanges in the inorganic species (14). Neither HNO nor



NO^+ could be observed spectrophotometrically in our reaction medium because of the absorption of N_2O_3 in the regions for each species. Nitrosyl hydride absorbs at 602, 709, and 757 $m\mu$ in the gas phase.²⁵ In the liquid phase this region is covered by the broad 635- $m\mu$ absorption of N_2O_3 . Nitrosonium ion absorbs in the region of 265 $m\mu$ (variable with H_2SO_4 concentration) in sulfuric acid solution.^{23a} This region is strongly absorbed by N_2O_3 below 300 $m\mu$. Because of the 635- $m\mu$ N_2O_3 absorption, 632.8- $m\mu$ laser Raman spectrophotometry could not be used in these studies.

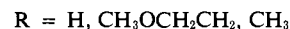
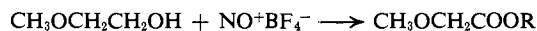
(22) The extinction coefficient for N_2O_3 in aqueous solution has not been reported. We have used the value of 20 as an approximation which Mason⁶ used in her studies on N_2O_3 -nonaqueous solvent systems.

(23) (a) N. S. Bayliss, R. Dingle, D. W. Watts, and R. J. Wilkie, *Aust. J. Chem.*, **16**, 933 (1963); (b) T. A. Turney and G. A. Wright, *J. Chem. Soc.*, 2415 (1958); (c) K. Singer and P. A. Vamplew, *ibid.*, 3971 (1956); (d) R. J. Gillespie, J. Graham, E. D. Hughes, C. K. Ingold, and E. R. A. Peeling, *J. Chem. Soc.*, 2504 (1950).

(24) An extinction coefficient of 50 for the 354 $m\mu$ absorption peak of nitrous acid was used for this estimation.¹⁸

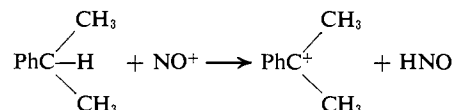
(25) S. W. Charles and G. C. Pimentel, *J. Chem. Phys.*, **37**, 2302 (1962).

In addition to our kinetic studies, further support for NO^+ as the oxidizing agent was gained from the reaction of nitrosonium fluoroborate with 2-methoxyethanol. This reaction was studied at 28° in acetonitrile; in 12 min methoxyacetic acid (1% yield), 2-methoxyethyl methoxyacetate (70% yield), and methyl me-



thoxyacetate²⁶ (0.1% yield) were products obtained from the oxidation of 2-methoxyethanol. These account for about 70–75% of the 2-methoxyethanol used. There was a very short period (45–60 sec) before gas evolution occurred.²⁷ The formation of products, the lack of an induction period, and the rapidity of the reaction all demonstrate that NO^+ can oxidize alcohols readily. By substituting 2-methoxyethanol for water in eq 6 of the reaction scheme, we see that the ester would be the expected major organic product.

Although nitrosonium ion is too weak an electrophile to attack an unactivated aromatic C–H bond, Olah and Friedman²⁸ have shown that isopropylbenzenes undergo a facile hydride-transfer reaction with nitrosonium salts from the tertiary C–H bond of the isopropyl substituent and yield a variety of products arising from the reactions of the dimethylphenylcarbonium ion. We



propose that in a completely similar manner, the oxidation of 2-methoxyethanol proceeds *via* hydride abstraction by nitrosonium ion from the C-1 and loss of a proton from the hydroxyl group to yield 2-methoxyethanol. A second hydride abstraction and proton loss from the hydrated aldehyde 2-methoxy-1,1-dihydroxyethane yields 2-methoxyacetic acid. The possibility that the hydride ion abstracted by nitrosonium ion is from the C-2 (even though the enol of the aldehyde would result) is eliminated by the large isotope effect observed for the oxidation of 2-methoxy-1,1-dideuterioethanol. In addition to NO^+ ,³⁰ HNO_3 , $H_2NO_3^+$, HNO_2 , $H_2NO_2^+$, N_2O_3 , $HN_2O_3^+$, NO_2 , NO_2^+ , and $CH_3OCH_2CH_2ONO$ should be considered as oxidizing agents. In our system, nitric acid, $H_2NO_3^+$, and NO_2^+ can be excluded at the outset because oxidation by any of these does not require an induction period. Although NO_2^+ may be able to abstract hydride from C-1, its concentration must be so low under our conditions that its reaction is not detectable. Miller³² concluded that the equilib-

(26) Methyl methoxyacetate and methyl nitrite (see Experimental Section) may be formed by the reaction of methanol with methoxyacetylum ion and NO^+ , respectively. Methanol may be formed by cleavage of methoxyethanol by HF liberated in the reaction. Methoxyethyl acetate may be formed by the reaction of methoxyethanol and acetonitrile in the presence of HF.

(27) A small amount of (0.1–1.8%) N_2O was produced in the HNO_3 system and in the $NO^+BF_4^-$ system, probably by the decomposition of HNO in a manner similar to the gas phase decomposition of HNO studied by Kohant and Lampe.²⁸



(28) F. C. Kohant and F. W. Lampe, *J. Amer. Chem. Soc.*, **87**, 5795 (1965).

(29) G. Olah and N. Friedman, *ibid.*, **88**, 5330 (1966).

(30) Nitrosonium ion has been proposed previously as the oxidizing agent in the nitric acid oxidation of formic acid¹⁸ and oxalic acid.³¹

(31) V. S. Koltunov, *Kinet. Katal.*, **9**, (5), 1034 (1968).

(32) D. J. Miller, *J. Chem. Soc.*, 2600 (1950).

rium constant for the ionization of nitrous acid by sulfuric acid is much greater than the corresponding ionization of nitric acid by sulfuric acid. In our system the estimated concentration of NO^+ is about 0.01 M so the corresponding NO_2^+ concentration must be much less. The concentration of H_2NO_2^+ in sulfuric acid solution has been demonstrated spectrophotometrically to be zero within experimental error or at most to exist at very low fractions of the HONO and NO^+ concentrations.^{23a} Nitrogen dioxide, though not detectable by us, must exist in some concentration since both N_2O_3 and HNO_3 can dissociate to give NO_2 . However, the NO_2 concentration decreases from the start as indicated by the transition in color of the solution from green to blue. This behavior is contrary to observed rates, if NO_2 were the oxidizing agent. Nitrous acid by itself or in dilute

acid solution readily forms nitrite esters with alcohols rather than act as an oxidizing agent. The nitrite ester can be considered a derivative of nitrous acid and, by itself, is sufficiently stable. Thus nitrous acid or the nitrite ester of methoxyethanol are probably not doing the oxidation. Dinitrogen trioxide in pentane acts as a nitrosating agent for alcohols so that species by itself is not an oxidizing agent.

Acknowledgment. We wish to thank R. A. Strojny and J. Crump for helpful discussions, R. A. Nyquist and V. B. Carter for infrared spectrophotometric interpretations and analyses, J. P. Heeschen and T. E. Evans for assistance in nmr interpretations, J. C. Tou and B. Hart for mass spectrometric analyses, and H. H. Grossman and B. I. Milner for computerized plotting of data.

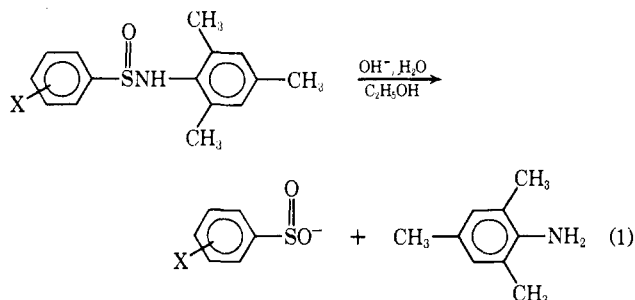
Hydrolysis of Arenesulfonamides in Basic Aqueous Ethanol. Nucleophilic Substitution at Tricoordinate Sulfur(IV)¹

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Abstract: Nine meta- and para-substituted *N*-mesitylbenzenesulfonamides were prepared and the kinetics of their reaction with hydroxide ion in aqueous ethanol studied. Second-order rate constants were obtained. The reaction was shown to be first order in base and first order in sulfonamide. Activation parameters were determined for the *p*-chlorobenzenesulfonamide as $\Delta H^\ddagger = +20.0$ kcal/mol and $\Delta S^\ddagger = -8.9$ eu. The rate constants gave a good correlation with Hammett's σ constants ($\rho = +1.3$). The procedure of Taft for determining specific resonance effects was applied to the data for the sulfonamides. A resonance value of -0.08 σ unit was obtained for *N*-mesityl-*p*-methoxybenzenesulfonamide indicating that the resonance contribution of the *p*-methoxyphenyl group to the resonance hybrid is slightly greater in the ground state than in the transition state. No significant resonance value ($+0.03$) was observed for the *p*-nitrophenyl substituent. The resonance contribution to the resonance hybrid for *N*-mesityl-*p*-nitrobenzenesulfonamide is of the same magnitude for both the ground state and the transition state. The lack of a significant resonance value for the *p*-nitrophenyl group argues against the formation of an addition intermediate. No incorporation of ^{18}O was found in unreacted *N*-mesityl-*p*-chlorobenzenesulfonamide isolated from a reaction mixture containing H_2^{18}O .

In recent years much attention has been given to the mechanistic aspects of nucleophilic substitution at di-, tri-, and tetracoordinate sulfur.³ In hope of contributing to this general subject, we have investigated a specific case of substitution at tricoordinate sulfur(IV),⁴ the basic hydrolysis of *N*-mesitylarenesulfonamides in aqueous ethanol (eq 1). Some other examples of trico-



(1) This work was supported by the National Science Foundation, Grants No. GP-5283 and GP-8136.

(2) This article is based on the Ph.D. Thesis of J. B. B., University of New Hampshire, 1968.

(3) For a discussion of nucleophilic substitution at sulfur as well as pertinent references, see (a) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 2731 (1970); (b) E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, **6**, 81 (1968); (c) E. Ciuffarin and G. Guaraldi, *J. Org. Chem.*, **35**, 2006 (1970); (d) J. L. Kice and G. J. Kasperek *J. Amer. Chem. Soc.*, **92**, 3393 (1970); (e) D. Landini, G. Modena, G. Scorrano, and F. Taddei, *ibid.*, **91**, 6703 (1969).

(4) The sulfur atom is named according to its coordination number (number of ligands not including unshared electrons) and its oxidation number (number of bonds to sulfur plus the formal charge on sulfur). See K. K. Andersen, S. A. Yeager, and N. B. Peynircioglu, *Tetrahedron Lett.*, 2485 (1970).

ordinate sulfur(IV) compounds which undergo nucleophilic substitution at sulfur are sulfoxides (R_2SO), sulfinyl chlorides (RSOCl), sulfilimines (R_2SNR), sulfonium salts (R_3S^+), and sulfinate esters (RS(O)OR). The various aspects of the substitution reactions can be conveniently divided into four categories: (1) the influence of the nucleophile's structure on reactivity, (2) the stereochemistry of the reactions, (3) the influence of the sulfur compound's structure on reactivity, and (4)