Nitration of Benzenesulfonate Ion in Acidic Nitrate Melts[1]

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Abstract: The nitration of benzenesulfonate and some benzenesulfonate derivatives in pyrosulfate–sulfate buffer solutions of $NaNO_3$–KNO_3 melts was studied in the temperature range 240–270°. Products of the reaction were determined by ion-exchange chromatography and ultraviolet spectrophotometry. The reaction follows pseudo-first-order kinetics in the presence of excess benzenesulfonate as measured by the decrease in melt acidity with time. The variation in observed rate as a function of benzenesulfonate and sulfate concentrations is consistent with a mechanism involving an intermediate $NO_2^+ \cdot BS^-$ complex. Based on a steady-state approximation for the concentration of this intermediate, several of the rate constants involved have been evaluated. Several aspects of the reaction not unambiguously defined by the kinetics are discussed, along with some preliminary findings on related reactions in substituted benzenesulfonate.

In recent years there has developed a substantial body of literature dealing with the chemistry of Lux–Flood acids in molten alkali nitrate solution, *e.g.*, Cu^{2+}, MoO_3, $Cr_2O_7^{2-}$, etc.[3-5] Although Jordan disputes the Lux–Flood acid–base theory as applicable to nitrate melts,[6] his group studied nitrate melts which were substantially basic. Upon reviewing the large number of reactions which have been studied in a nitrate melt solvent, it is apparent that in acidic nitrate melts acid–base reactions are best described by the transfer of oxide ions from bases to acids. One of the strongest acids in nitrate melts is the pyrosulfate ion, $S_2O_7^{2-}$. Duke and Yamamoto[7] and later Kust and Duke[8] studied the solvolysis of $S_2O_7^{2-}$ in alkali nitrate melts. Their studies suggest that appreciable concentrations of nitronium ion, NO_2^+, can be achieved and maintained in nitrate melts strongly buffered with sulfate. This conclusion gains significance in view of the role postulated for NO_2^+ in nitration. As early as 1903 Von Euler[9] proposed that NO_2^+ was the actual species involved in nitrations in sulfuric–nitric acid mixtures. Since then cryoscopic measurements on that acid mixture, studies of nitric acid nitrations in other acidic solvents, and more recently nitrations employing stable nitronium salts, *e.g.*, $NO_2^+BF_4^-$,[10,11] have served to confirm the postulate. The availability of NO_2^+ in nitrate melts therefore presented the possibility of studying nitrations in a new and relatively unusual solvent.

Several groups have reported nitrations based on acidic nitrate melts as a source of NO_2^+. Fay, Temple, and Williamson[12] passed benzene, toluene, and several other substrates through nitrate melts containing high concentrations of pyrosulfate and obtained variable yields of nitration products. Kennedy and Buse,[13] in an attempt to increase yields by increasing the contact time between substrate and melt, passed substrate vapors through a heated column containing the acidified nitrate melt absorbed on crushed firebrick. They too reported variable yields, although in one case the yield of nitrotoluene was greater than 100% based on the amount of acid used.

These studies, while providing additional evidence for the existence of appreciable concentrations of nitronium ion in acidic nitrate melts, suffered from a lack of reproducibility. Being interested in a more quantitative method of investigating nitrations in molten nitrates, we were led to the present work by an observation made by Duke. Duke[14] reported that solutions of sodium benzenesulfonate in sodium–potassium nitrate eutectic melts evolved small amounts of nitrobenzene. Our attempts at duplicating this result indicated that in the absence of acid the benzenesulfonate ion (BS^-) was both soluble and stable in nitrate melts up to 300° for 48 hr. When pyrosulfate, metaphosphate, or molybdenum(VI) oxide were added to these solutions, there was an immediate reaction evolving NO_2, nitrobenzene, and other products. Since the reaction of pyrosulfate in molten nitrates had been previously well characterized, and the analysis of the acidity of pyrosulfate-containing melts involved only simple titration, we have confined the majority of our work to that acid. Benzenesulfonate was the substrate most extensively studied, although substituted benzenesulfonates have been found to undergo similar reaction.

Experimental Section

Reagents. Sodium benzenesulfonate and sodium *m*-nitrobenzenesulfonate were Eastman practical grade, recrystallized from methanol. *o*- and *p*-nitrobenzenesulfonic acids were obtained from Pfaultz and Bauer, Flushing, N. Y., and were neutralized with sodium hydroxide, the solution was filtered, and the salts were crystallized from 80% aqueous methanol. Both were found to be free of extraneous isomers by ion-exchange chromatography.

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Sodium *m*-benzenedisulfonate was prepared from the purified barium salt by reaction with sodium sulfate, followed by recrystallization from 90% aqueous methanol. Potassium pyrosulfate was reagent grade material which after drying at 125° assayed 35.5% as sulfuric acid by titration. Dowex 2 × 8, 200–400 mesh, was air-dried at 50° and sieved, and the fraction between 45- and 60-μ diameter was retained. This fraction was purified by treatment in turn with 10% NaOH solution, distilled water, 95% ethanol, 3 *N* HCl in 50% ethanol, and distilled water until the final distilled water rinse had no appreciable ultraviolet absorbance above 240 nm. The purified material was stored moist until used. All other chemicals used were of reagent grade, and those used in the molten salt system were stored in an oven at 125° until used.

Apparatus. All of the kinetic studies and a majority of the other molten-salt reactions were carried out in reaction vessels immersed in a molten nitrate constant temperature bath. The reaction vessel which proved most convenient consisted of a Pyrex cylinder approximately 6-cm o.d. by 15 cm, having a medium porosity sintered glass disk sealed about 1 cm from the lower end and a standard taper 14/20 outer joint at the top. A tube for the introduction of gas was led into the chamber below the sintered glass disk. This flask can be immersed nearly to the neck in the salt bath, ensuring good thermal contact and allowing for adequate preheating of sweep gas. Samples of the melt could be withdrawn through the standard taper joint, or a trap could be fitted for the collection of volatile products of the reaction. Traps were of a simple U-tube design with a glass wool plug at the outlet to scrub any aerosols formed.

Volumetric analysis for residual acid, volatile acid, water, and sulfate was performed with a Photovolt pH meter, Beckman aquameter, and an A. H. Thomas Co. Carius sulfate titration apparatus, respectively. Ion-exchange separations of the sulfonates in melt samples were performed using jacketed glass columns of 6.5- or 30-cm length, a Milton Roy Co. minipump, and a Misco 6000 fraction collector.

Spectrophotometric analyses of ion-exchange fractions and of nitrobenzene were run on a Cary 14 spectrophotometer using 1-cm matched silica cells. Molar absorptivities of the sulfonates were determined on an Hitachi EPS-3T spectrophotometer. In later work the fraction collector was replaced by a Beckman DB spectrophotometer and strip chart recorder.

Procedure. In all runs temperature of the bath was adjusted at least 24 hr prior to the actual run and rechecked before and after the run. No drift was ever observed. Fifty grams each of sodium and potassium nitrate and the required amounts of sodium sulfate and sodium benzenesulfonate were weighed out on a torsion balance ±5 mg, combined and ground briefly in a mortar, and transferred into the reaction vessel. A flow of 50 ± 5 ml/min of dry nitrogen was started and the vessel then lowered into the salt bath. Melting and dissolution of the salts were usually complete within 0.5 hr. The nitrogen flushing was continued for at least an additional 0.5 hr and the required amount of powdered potassium pyrosulfate then added.

In those reactions to be analyzed for volatile products, the vessel was closed with a trap cooled in an acetone–Dry Ice bath. After reaction the contents of the trap were rinsed with dry methanol into a volumetric flask and diluted to volume. The resulting solution was analyzed for water, acidity, and nitrobenzene.

For the study of the kinetics of the acid in the melt, the melt was vigorously stirred for 1 min after the addition of the pyrosulfate, using a preheated pipet. This same pipet was used for the withdrawal of samples at regular intervals throughout the reaction, as it was found that use of a fresh pipet for each sample introduced too much error in the temperature of the melt. The melt samples, approximately 5 g, were quenched in the cavities of a porcelain spot plate. After cooling to room temperature the resulting pellets were weighed on an analytical balance, dissolved in 50 ml of distilled water, and titrated to pH 7.0 ± 0.05 with 0.0100 *N* NaOH. The resulting solution could then be quantitatively transferred to a 100-ml volumetric flask and brought to volume with purified water. An aliquot of this solution could then be analyzed for sulfate and a second aliquot concentrated for ion-exchange analysis[15] of the sulfonates.

The rate of generation of NO_2 was determined by flushing the NO_2 from the reaction vessel into a flow cell with 50 ml/min of N_2. The absorbance of the NO_2 at 435 nm as a function of time was determined using a Spectronic 20 spectrophotometer. Calculations based on the dissociation constant of N_2O_4 indicated that the concentration of the nonabsorbing dimer was small enough to be neglected without materially affecting the accuracy of the determination.

Results

The observed overall rate of decrease of acidity was found to follow pseudo-first-order kinetics in the temperature range 240–270° at all sulfate concentrations as long as BS^- was either completely absent or present in greater than twofold excess of the acid. In the intermediate range second-order kinetics were observed, but the difficulty of accurately determining small concentrations of BS^- in the presence of a large excess of nitrate prevented quantitative treatment of these results. For runs involving excess BS^- the observed values of acidity as a function of time were fitted by a least-squares program[16] to a first-order relationship, and the calculated rate constant and correlation coefficient obtained. The rate constants obtained, representing the average of from two to five runs, are tabulated in Table I. The rate of acid loss is seen to increase rapidly with increasing BS^- at first and more slowly at higher BS^- concentrations, and to decrease essentially linearly with increasing sulfate concentration.

Table I

SO_4^{2-}, *M*	BS^-, *M*	$10^3k'$, sec^{-1}			
		240°	250°	260°	270°
0.05	0	0.66			
	0.05	1.6			
	0.10	2.5			
	0.15	2.8			
0.10	0	0.44	0.56	0.76	
	0.05	1.2	1.85	2.4	
	0.10	1.6	3.7	3.2	
	0.15	1.8	4.05	3.6	
	0.20			4.8	
0.15	0	0.32	0.33	0.45	0.80
	0.05	0.74	1.6	2.05	2.90
	0.10	1.1	2.05	2.45	4.95
	0.15		2.7	3.05	6.4
	0.20			3.0	6.6
	0.25				7.5
0.20	0		0.22	0.6	0.65
	0.05		1.2	1.75	2.55
	0.10		2.0	2.4	3.65
	0.15		2.2	3.4	4.95
	0.20			3.65	6.3
	0.25				7.15
0.25	0				0.45
	0.05				2.6
	0.10				3.65
	0.15				3.9
	0.20				4.7

The rate of appearance of NBS^- was followed by ion-exchange chromatography of aqueous solutions of melt samples after titration for acidity. Typical results are presented in Table II. While the precision of this method is adequate for semiquantitative work, it is not sufficient to allow calculation of a reliable rate expression for appearance of NBS^-. The concentration of NBS^- is seen to increase rapidly at first, but within a few minutes the increment in NBS^-

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(15) J. Robinson and J. Schlegel, to be submitted for publication.

(16) Hewlett-Packard Co., 9100 B Calculator Program Library, program 70803.

Table II. Concentration of Total Nitrobenzenesulfonates as a Function of Time

$[SO_4^{2-}]$	$[BS^-]$	t, sec	T = 260°	T = 270°
0.15	0.15	60	5.4×10^{-3} M	6.0
		120	6.5	7.2
		180	7.4	7.7
		240	8.0	8.0
		300	8.1	8.4
		360	8.4	8.4
		720	9.0	8.7
				T = 240°
0.15	0.10	120	5.2	0.0055
		180	6.0	0.0065
		240	6.6	0.0067
		300	7.3	0.0069
		360	7.4	0.0076
		720	8.7	0.0093

becomes smaller than the relative error in the analytical method. The data are nevertheless qualitatively in agreement with data for acid loss rate, and we will therefore base arguments pertaining to NBS^- appearance rate on the more accurately known acid disappearance rate.

The rate of generation of NO_2 was also studied and found to correspond closely with the overall rate of acid loss, as indicated in Table III. This result is not unexpected as the two mechanisms of acid loss involve nitration and solvolysis, and nitration has already been shown to give the same rate as overall acid loss.

Table III. Comparison of the Rate of NO_2 Formation with Overall Rate of Acid Loss

$[SO_4^{2-}]$, M	$[BS^-]$, M	T, °C	$d \ln [NO_2]/dt \times 10^3$, sec^{-1}	$d \ln A_t/dt \times 10^3$, sec^{-1}
0.20	0.15	270	5.0	5.0
0.20	0.10	270	4.0	3.7
0.15	0.15	270	6.2	6.4

Duke and Yamamoto[7] found that the rate of solvolysis of NO_2^+ was increased by an increase in the flow rate of inert gas through the melt. In our work we have confirmed this observation for systems containing no BS^-. No change is observed in overall acid loss rate in going from 0 to 50 ml/min of N_2 in systems containing BS^-. This is rather surprising in view of the more effective dispersion of gas in these systems due to the surfactant properties of BS^- in nitrate melts. More surprising however is the effect on yield of nitrobenzene (NB) in changing from flow rates of 50 ml/min or less to 100 ml/min. The results in Table IV indicate that production of nitrobenzene is almost completely inhibited at the higher flow rate, and that the effect is common to melts acidified with pyrosulfate and metaphosphate, while nitration to NBS^- is largely limited to melts containing pyrosulfate. At present we are unable to provide a viable explanation of this flow-rate dependence.

Table IV. Nitrobenzene Yield as a Function of Nitrogen Flow Rate

T, °C	Acid, mmol	N_2 flow rate, ml/min	Yields, mmol HNO$_3$	NB	NBS
250	$S_2O_7^{2-}$, 3.5	100	2.35	0.2	1.9
250	S_2O_7, 3.5	0	2.55	2.35	2.3
250	$(NaPO_3)_x$, 10	100	0.1	0.04	Trace
250	$(NaPO_3)_x$, 10	0	0.2	1	Trace

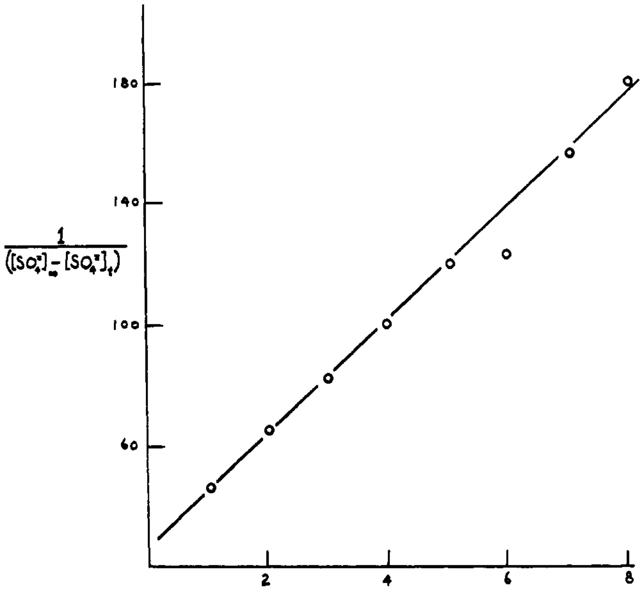

Figure 1. Rate of formation of sulfate.

Another interesting feature of the NB production rate is illustrated in Table V, in which the yield of NB is calculated after 12 min of reaction time. The yield is based upon the difference between initial BS^- concentration and the sum of recovered BS^- and NBS^-. It is apparent that NB yield is proportional to the square of the initial BS^- concentration, and a second-order rate constant can be calculated which is reasonably constant considering the precision of the ion-exchange data on which it is based. Further confirmation of the second-order dependence on BS^- is provided by data on the rate of appearance of sulfate in the melt, plotted in Figure 1. It is also found that the rate constants given in Table V are inversely proportional to sulfate concentration.

Table V. Rate of Nitrobenzene Formation as a Function of BS^- Concentration

T, °C	$[SO_4^{2-}]$, M	$[BS^-]_0$, M	$[BS^-]_{720}$,[a] M	$k'' \times 10^3$, $M^{-1}\,sec^{-1}$
260	0.10	0.05	0.045	3.08
	0.10	0.10	0.0807	3.32
	0.10	0.15	0.111	3.25
	0.15	0.05	0.046	2.42
	0.15	0.10	0.087	2.08
	0.15	0.15	0.114	2.92
	0.15	0.20	0.148	2.44

[a] $[BS^-]_{720}$ is the concentration of total sulfonates at 720 sec.

Discussion

The following mechanism is proposed to account for the observed variation in overall rate of acid loss with changes in sulfate and BS^- concentration.

Table VI. Relative Magnitudes of k_5 and k_8

T, °C	$\frac{k_8}{k_3(k_4 + k_9)}$	$\frac{k_5}{k_3(k_4 + k_9)}$	$\frac{k_{-3} + k_4 + k_9 + k_8[\mathrm{BS}^-]}{k_3(k_4 + k_9)}$	$[\mathrm{BS}^-]$, M	$\frac{k_{-3} + k_4 + k_9 + k_5[\mathrm{SO_4}^{2-}]}{k_3(k_4 + k_9)}$	$[\mathrm{SO_4}^{2-}]$, M
240	500	600	22	0.05	37	0.05
250	250	240	13	0.05	27	0.10
260	230	150	13	0.05	22	0.15
270	90	130	9	0.10	18	0.15

$$\mathrm{S_2O_7}^{2-} + \mathrm{NO_3}^- \overset{K}{\rightleftharpoons} \mathrm{NO_2}^+ + 2\mathrm{SO_4}^{2-} \qquad \text{rapid equilibrium} \tag{1}$$

$$\mathrm{NO_2}^+ + \mathrm{NO_3}^- \xrightarrow{k_2} 2\mathrm{NO_2} + \mathrm{O} \tag{2}$$

$$\mathrm{NO_2}^+ + \mathrm{BS}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (\mathrm{NO_2}^+ \cdot \mathrm{BS}^-) = \mathrm{C} \tag{3}$$

$$\mathrm{C} \xrightarrow{k_4} \mathrm{NBS}^- + \mathrm{H}^+(\mathrm{solv}) \tag{4}$$

$$\mathrm{C} + \mathrm{SO_4}^{2-} \xrightarrow{k_5} \mathrm{BS}^- + \mathrm{NO_3}^- + (\mathrm{SO_3}) \tag{5}$$

$$(\mathrm{SO_3}) + \mathrm{SO_4}^{2-} \xrightarrow{k_6} \mathrm{S_2O_7}^{2-} \tag{6}$$

$$2\mathrm{H}^+ + 2\mathrm{SO_4}^{2-} \longrightarrow \mathrm{H_2O} + \mathrm{S_2O_7}^{2-} \tag{7}$$

$$\mathrm{C} + \mathrm{BS}^- \xrightarrow{k_8} \mathrm{NB} + \mathrm{SO_3} + \mathrm{BS}^- \tag{8}$$

$$\mathrm{C} + \mathrm{NO_3}^- \xrightarrow{k_9} \mathrm{BS}^- + 2\mathrm{NO_2} + \mathrm{O} \tag{9}$$

Applying a steady-state approximation to calculate the concentration of the complex, C, in terms of the rate constants for the individual steps we obtain

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = 0 = k_3[\mathrm{NO_2}^+][\mathrm{BS}^-] - k_{-3}[\mathrm{C}] - k_5[\mathrm{C}][\mathrm{SO_4}^{2-}] - k_8[\mathrm{C}][\mathrm{BS}^-] - k_9[\mathrm{C}]$$

and the steady-state concentration is given by

$$[\mathrm{C}]_{\mathrm{ss}} = \frac{k_3[\mathrm{NO_2}^+][\mathrm{BS}^-]}{k_{-3} + k_4 + k_5[\mathrm{SO_4}^{2-}] + k_8[\mathrm{BS}^-] + k_9}$$

The overall rate of loss of acid can be expressed as

$$\frac{\mathrm{d}\ln[\mathrm{A}]}{\mathrm{d}t} = \frac{\mathrm{d}\ln[\mathrm{NO_2}^+]}{\mathrm{d}t} = k' = k_2 + \frac{k_4 + k_9k_3[\mathrm{BS}^-]}{k_{-3} + k_4 + k_9 + k_5[\mathrm{SO_4}^{2-}] + k_8[\mathrm{BS}^-]}$$

This expression is seen to be qualitatively in agreement with the observed inverse dependence of rate on sulfate and the combined direct and inverse dependence on BS^-.

The hypothesis of a $\mathrm{NO_2}^+ \cdot \mathrm{BS}^-$ complex is based upon the following evidence. First, the dependence on the inverse sulfate concentration indicates that equilibrium 1 does not directly govern the concentration of the reactive intermediate. Since this equilibrium does participate in the concentration of free nitronium ion, the observed sulfate dependence indicates that the rate of reaction of free nitronium ion must be much smaller than that of the complex. Second, the observed rate of formation of $\mathrm{NO_2}$ is much greater than can be accounted for by solvolysis of free nitronium ion, and increases directly with increase in BS^-, even at low BS^- concentrations. This indicates that BS^- is involved in the species undergoing solvolysis, and that this species contains $\mathrm{NO_2}^+$ in a form which undergoes solvolysis more readily than free nitronium ion. The correspondence between the rate of generation of $\mathrm{NO_2}$ and the overall rate of loss of acid indicates that the two reactions leading to acid loss, reactions 4 and 9, either involve a common intermediate or species which are rapidly generated from a common intermediate. Finally, the insensitivity of the solvolysis and nitration reactions to the flow rate of inert gas is in contrast to the substantial dependence observed in the solvolysis of free nitronium ion in the absence of BS^-. This again indicates that free nitronium ion plays at most a small role in the overall reaction.

The relative magnitudes of the rate constants are obtained by plotting the equation

$$\frac{[\mathrm{BS}^-]}{k' - k_2} = \frac{k_{-3} + k_4 + k_9 + k_5[\mathrm{SO_4}^{2-}] + k_8[\mathrm{BS}^-]}{k_3(k_4 + k_9)}$$

A plot of $[\mathrm{BS}^-]/(k' - k_2)$ *vs.* $[\mathrm{BS}^-]$ holding $[\mathrm{SO_4}^{2-}]$ constant gives a series of lines of slope $k_8/[k_3(k_4 + k_9)]$ and intercept $(k_{-3} + k_4 + k_9 + k_5[\mathrm{SO_4}^{2-}])/[k_3(k_4 + k_9)]$. Similarly a plot of the same quantity *vs.* $[\mathrm{SO_4}^{2-}]$ holding $[\mathrm{BS}^-]$ constant yields a series of lines of slope $k_5/[k_3(k_4 + k_9)]$ and intercept $(k_{-3} + k_4 + k_9 + k_8 \cdot [\mathrm{BS}^-])/[k_3(k_4 + k_9)]$. These data are tabulated in Table VI. The product $k_5/[k_3(k_4 + k_9)]$ times $[\mathrm{SO_4}^{2-}]$ for each temperature gives a value which is very close to the value reported for $(k_{-3} + k_4 + k_9 + k_5[\mathrm{SO_4}^{2-}])/[k_3(k_4 + k_9)]$. Also the product $k_8/[k_3(k_4 + k_9)]$ times $[\mathrm{BS}^-]$ for each temperature gives a value which is very close to the value reported for $(k_{-3} + k_4 + k_9 + k_8[\mathrm{Bs}^-])/[k_3(k_4 + k_9)]$. This observation indicates that the quotient $(k_{-3} + k_4 + k_9)/[k_3(k_4 + k_9)]$ in each case is small, on the order of ten or less. Since k_4 and k_9 are presumed to be involved in the rate-limiting steps, they should be much smaller than k_3. This indicates then that k_{-3} is not greater than ten times $k_3(k_4 + k_9)$, and if $k_4 + k_9$ is assumed small with respect to k_3, this further indicates that k_3 is of the order of 1, since the term $1/k_3$ can be separated from the residual and thus cannot be greater than the full residual.

The above derivations are based on the assumptions that sulfate and BS^- concentrations are essentially unchanged in the course of a given reaction. This is rather a large assumption in several cases, but must be accepted for the moment. Attempts to account for the changing sulfate and BS^- concentrations as determined by our present analytical methods did not improve the results materially, but did reduce the data scatter.

In obtaining the relative magnitudes of the several rate constants, values of k_3 from 0.1 to 10 M^{-1} sec^{-1} were used in a computer routine to determine the most consistent value for this constant. Other constants are based on this optimum value. Assuming a value of 1.0 M^{-1} sec^{-1} for k_3, the ratios $k_5/(k_4 + k_9)$ and $k_8/(k_4 + k_9)$ are found to be approximately equal and of the order of 2 × 10^2 at 260°. This allows the expression of the observed rate to be written in terms of $k_4 + k_9$ and k_3.

$$k' = k_2 + \frac{k_3(k_4 + k_9)[\mathrm{BS^-}]}{k_{-3} + k_4 + k_9 + 230(k_4 + k_9)[\mathrm{SO_4{}^{2-}}] + 150(k_4 + k_9)[\mathrm{BS^-}]}$$

The previously cited intercept data indicate k_{-3} is of the order of $10(k_4 + k_9)$. Rearranging terms, $k'(10 + 1 + 230[\mathrm{SO_4{}^{2-}}] + 150[\mathrm{BS^-}]) = [k_2/(k_4 + k_9)] + k_3[\mathrm{BS^-}]$. At 260^c, this yields $(k_4 + k_9) = 10^{-2}$. From the relative yields of NO_2 and NBS^-, Table VII, k_4 and k_9 are found to be nearly equal at this temperature, and thus each is of the order of 5 × 10^{-3} sec^{-1} at 260°. This in turn indicates that k_5 and k_8 are of the order of 1 M^{-1} sec^{-1} at 260°.

Table VII. Relative Yields of Nitrogen Dioxide and Nitrobenzenesulfonate

T, °C	$[\mathrm{SO_4{}^{2-}}]$, M	$[\mathrm{BS^-}]$, M	NO_2, mmol	NBS^-, mmol
240	0.05	0.05	0.5	1.0
		0.10	0.6	1.20
		0.15	0.6	1.15
	0.10	0.10	0.45	1.02
		0.15	0.45	1.01
	0.15	0.05	0.35	0.60
		0.10	0.35	1.00
260	0.10	0.05	0.85	0.70
		0.10	0.7	1.07
		0.15	0.7	1.09
	0.15	0.05	0.80	0.75

The relative magnitudes of these constants indicate that the measured acidity is in rapid equilibrium among the species NO_2^+, $S_2O_7^{2-}$, $NO_2^+\cdot BS^-$, $SO_3\cdot BS^-$, and HSO_4^-. The position of this equilibrium depends upon the rate of reaction of the $SO_3\cdot BS^-$ complex, for which we have at present no evidence. The maintenance of a rapid equilibrium among the acidic species is confirmed by experiments in which the acid was introduced as gaseous SO_3 rather than $S_2O_7^{2-}$. Within experimental error the rate was identical with that obtained under the same conditions using $S_2O_7^{2-}$.

This rapid equilibrium among the acidic species allows us to justify an assumption implicit in the data treatment used. The term $[NO_2^+]$ appears in the expression for the steady state $NO_2^+\cdot BS^-$ complex concentration, whereas the analytical quantity determined is total melt acidity. The observed rate is thus $(\mathrm{d[acid]_{total}}/\mathrm{d}t)$. If we express the NO_2^+ concentration as $K[\mathrm{A}]_{\mathrm{total}}$, where K is the overall equilibrium constant and includes terms involving $[\mathrm{SO_4{}^{2-}}]$ and $[\mathrm{BS^-}]$, then

$$k' = \frac{\mathrm{d[A]_T}}{\mathrm{[A]_T\,d}t} = \frac{\mathrm{d}K\mathrm{[A]_T}}{K\mathrm{[A]_T\,d}t} = \frac{\mathrm{d[NO_2{}^+]}}{\mathrm{[NO_2{}^+]\,d}t} = \frac{\mathrm{d\,ln\,[NO_2{}^+]}}{\mathrm{d}t}$$

The unknown NO_2^+ concentration is thus eliminated from the kinetic expression.

The values of the constants found above confirm the validity of the steady-state approximation used. k_3 is approximately 100 times larger than k_{-3} and of approximately the same magnitude as k_5 and k_8. k_3, k_5, and k_8 are all larger by at least an order of magnitude than k_4 and k_9, which control the rate of disappearance of acid. The rate of disappearance of acid is thus much slower than the rate of equilibration among the acidic species, and the approximation of a steady-state complex concentration is reasonable.

The rate of formation of nitrobenzene in terms of this mechanism is

$$\frac{\mathrm{d[NB]}}{\mathrm{d}t} = k_8[\mathrm{C}]_{\mathrm{ss}}[\mathrm{BS^-}] = \frac{k_8k_3[\mathrm{NO_2{}^+}][\mathrm{BS^-}]^2}{k_{-3} + k_4 + k_9 + k_5[\mathrm{SO_4{}^{2-}}] + k_8[\mathrm{BS^-}]}$$

The experimentally determined constant at 260° with respect to $[\mathrm{BS^-}]^2$ is 3.2 × 10^{-3} M^{-1} sec^{-1} at 0.1 M SO_4^{2-} and 2.5 × 10^{-3} M^{-1} sec^{-1} at 0.15 M SO_4^{2-}. Substituting the previously determined constants we find that the pseudo-steady-state concentrations of $[NO_2^+]$ are 4.5 and 2.8 × 10^{-4} M, respectively, using $[\mathrm{BS}]^- = 0.10$ M for each. These concentrations are an order of magnitude lower than those calculated for the same total acid concentration using the equations of Kust and Duke for the pyrosulfate solvolysis equilibrium. This discrepancy again indicates that the pyrosulfate solvolysis is not controlling the concentration of free NO_2^+ and that the observed acidity of the melt is held predominantly as a more basic species such as the postulated complex of SO_3 with BS^-. Substitution of these values of $[NO_2^+]$ into the expression for the steady-state concentration of the $NO_2^+\cdot BS^-$ complex gives a value of approximately 10^{-5} M, also indicating that the acid is present almost exclusively as the postulated $SO_3\cdot BS^-$ complex.

A point not previously covered is the formation of styphnic acid (2,4,6-trinitroresorcinol). Barvinskaya and Spryskov[17] have studied the nitration of benzenesulfonic acid in sulfuric acid–nitric acid mixtures, and have proposed that the formation of styphnic acid in their system results from initial oxidation of the BS^- to a phenolsulfonate, followed by rapid nitration, desulfonation, and further oxidation to the final product. We feel that this is also the case in our system, the oxidation resulting from the oxygen generated in the solvolysis of NO_2^+. The choice of the oxidizing agent is based on the observation that styphnic acid production occurs almost solely during the first minute of reaction, when the pyrosulfate is still dissolving and locally high concentrations of acid are undergoing rapid solvolysis. After the acid becomes evenly distributed the solvolysis rate decreases greatly and the production of styphnic acid ceases. The concentration of styphnic acid in the melt reaches a maximum of approximately 0.002 M and then decreases slowly by volatilization in the nitrogen stream. The yield of styphnic acid is rather variable but always small, and thus its effect on acid loss rate after the first minute of reaction has been neglected.

Finally, preliminary work on substituted benzenesulfonates indicates that the general reactions observed for benzenesulfonate occur to a greater or lesser extent in a wide variety of substrate systems. In the more active substrates such as toluenesulfonate, reaction is very rapid and nitration appears to predominate over nitration–desulfonation. In less active sub-

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strates, *e.g.*, nitrobenzenesulfonate, chlorobenzenesulfonate, and particularly *m*-benzenedisulfonate, the desulfonation mechanism predominates. In fact we have found that for *m*-benzenedisulfonate, desulfonation is virtually the sole mechanism of nitration. It is interesting to note that the overall observed rate of acid loss for systems containing *m*-benzenedisulfonate is nearly the same as that for the corresponding BS$^-$ systems at low substrate concentrations, but the leveling off of the rate at higher *m*-BDS concentrations is much more pronounced. We hope that complete studies of the reactions of these substituted benzenesulfonates may help to further elucidate the mechanisms involved in nitration in acidic nitrate melts.

Mechanistic Studies of Chemical Exchange Reactions by Complete Nuclear Magnetic Resonance Line-Shape Fitting. I. General Aspects

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Abstract: In any chemical exchange reaction which modifies nuclear magnetic resonance line shapes the spectrum can be computed from a set of pseudo-first-order rate constants arranged in matrix form, provided the line widths in the absence of exchange are accessible experimentally. The spectrum is a sensitive analytical tool in prescribing or eliminating possible reaction mechanisms. The rate matrix formed from the pseudo-first-order rate constants may correspond to a truncated or nontruncated exchange system. In the nontruncated cases all resonances are above the noise level of the spectrometer and in the region where frequency differences are modulated randomly by chemical exchange effects. In truncated systems contributions to line shapes occur also from resonances which are unobservable and which must therefore be included in terms of other measurable parameters in the rate matrix. The information available regarding reaction mechanism is discussed for both cases and the number of pseudo-first-order rate constants which may be independently determined is derived.

The study of chemical-exchange phenomena in modifying line shapes of nuclear magnetic resonance (nmr) spectra is highly developed both from the theoretical and experimental points of view.[2-16] At this point most applications of the technique have been accomplished in the study of hindered-rotation barriers or ring-inversion phenomena, where for the most part the mechanism of the kinetic process is either not in doubt[3,5,7,8,14-17] or resolves itself into simple alternatives.[18-20] In cases where the mechanism of the intramolecular process is known emphasis has been placed upon the precision of the measured rate constants and their variation with temperature, solvent, and concentration. The derived kinetic parameters such as energy, entropy, and free energy of activation have provoked a great deal of controversy[5,7,8,14,15] because the measurement of true line shapes is so difficult and different laboratories have not successfully agreed in most cases on the derived kinetic parameters. Very recently, some thorough studies have been made with a full analysis of systematic and random errors encountered in the experiment.[21-23] It is important to include all sites contributing to the exchange, variation of chemical shift and spin coupling with temperature, a careful monitoring of the Lorentzian line shape of an included line-shape standard, and a well defined temperature measurement, and to satisfy all conditions inherent in the slow passage Bloch equations.[24] If sufficient care is exercised in the experiment and the analysis, a full line-shape fit should deviate less than 1.5% over 100 data points in the spectrum, chosen so as to emphasize possible deviations.

Now that the experimental conditions can be reproduced in cases where the mechanism of a chemical process is known the present work seeks to investigate the power of the technique in deciding the mechanism of a chemical reaction in cases where this is unknown. In

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