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MASTER

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FIRST QUARTERLY TECHNICAL SUMMARY REPORT
ON THE HOMOGENEOUS PRODUCTION AND
REMOVAL OF NO_x FROM COMBUSTION
EXHAUST FLOWS

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Prepared by:

Joel A. Silver

Center for Chemical and Environmental Physics
AERODYNE RESEARCH, INC.
Bedford Research Park
Crosby Drive, Bedford, MA 01730

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ABSTRACT

Initial work on discerning the effect of sulfur-bearing compounds on the NH_i/NO_x chemical system in combustor exhaust flows has begun. A comprehensive survey of pertinent sulfur chemistry was initiated and experiments to measure the global formation rate of NO in reactions of $\text{SO}_2 + \text{NH}_i$ ($i = 1, 2, 3$) were planned.

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1. INTRODUCTION

The production and removal of NO_x and other combustion products during fossil fuel combustion is a serious environmental problem for both stationary and mobile driven energy systems. Since stationary systems are faced with increased utilization of coal, oil shale, or synthetic fuel oils, all of which have significant levels of fuel-bound nitrogen, NO_x formation may become acute.

Recent studies of the production of NO_x due to oxidation of fuel nitrogen indicate that a critical role is played by the interaction of NH_i ($i=1,2,3$) species with NO , O_2 , OH , and H . In fact, these reactions play a vital role in the homogeneous removal of NO_x from combustion exhaust streams upon addition of NH_3 or NH_3 -like compounds. Over the past two years, there has been an increased understanding of the chemistry of the NH_i/NO_x system at combustor exhaust temperatures. For an ammonia addition system to be effective in reducing NO_x emissions, it must work successfully in the presence of a variety of sulfur-bearing compounds present in the products of combusted coal and oil shale.

The work in progress has three major objectives. The first objective is to determine whether the reactions of SO_2 (the predominant sulfur-bearing compound present) + NH_i ($i=1,2,3$) directly produce NO_x in the temperature range of 300 - 1500 K (Task 1). As these reactions are of key importance, all other products of these reactions will also be identified (Task 2). Depending on the products and value of these rate constants, the effectiveness of NO removal by NH_3 could be dramatically affected.

The second objective is to screen and evaluate various sulfur-containing scavenger precursors such as SO , SO_2 , HS , and H_2S to assess their impact on the NH_i/NO_x chemical system (Task 3). This will involve an evaluation of published experimental and theoretical rates for all pertinent reactions. For those key reactions where the data is either insufficient or nonexistent, the

detailed constants rate will be measured using the High Temperature Fast Flow Reactor (HTFFR) facility at ARI (Task 4).

The third objective involves the evaluation and impact of the kinetic data on the effectiveness of NO removal by ammonia addition in the presence of sulfur-bearing compounds at combustor exhaust gas temperatures. This will be accomplished by modeling the process using Aerodyne's PACKAGE code (Task 5). This will allow a complete evaluation of the combined $\text{NH}_3/\text{SO}_x/\text{NO}_x$ chemical system on the abatement of NO emissions.

2. TECHNICAL SUMMARY PROGRESS REPORT

A summary of progress achieved during the last quarter is presented below. A time-phasing schedule for each task is shown in Fig. 2.1.

Task 1: Measurement of Global NO Formation Rate Constants

The purpose of this task is to measure the global rate constant for the formation of NO from the reactions of NH_i ($i=1,2,3$) with SO_2 over the temperature range 300 - 1500 K. The NO resonance lamp used to detect NO has been assembled and installed in the fast flow reactor. The required inlet lines for SO_2 have been assembled and the rate measurements will begin shortly.

Task 3: Screen and Evaluate Key Sulfur-Containing Species and Reactions

The major effort during this quarter was the compilation of published thermodynamic and reaction rate data for all sulfur-bearing species which may possibly exist in combustor exhaust flow. These reactions are being evaluated to determine which ones are potentially important to the $\text{NH}_i/\text{NO}_x/\text{SO}_x$ chemical system. Reactions which have not been previously studied, but are possibly important are also identified.

Task 5: Computer Model for $\text{NH}_i/\text{NO}_x/\text{SO}_x$ Chemistry

The existing model for NH_i/NO_x chemistry previously developed is being expanded to include the key rates identified in Task 3. Once completed, the effect of SO_x on the chemistry will be tested.

Figure 2.1 Contract Task Schedule

3. GLOBAL FORMATION RATES OF NO

3.1 Task Goals and Milestones

The goals of this task are to provide global rate constants for the formation of NO from the following reactions over the temperature range of 300 - 1500 K.

The NO is to be detected using resonance fluorescence techniques. The detection system has been assembled and tested. Calibration of the resonance lamp is underway.

3.2 Technical Discussion

Using the Aerodyne High Temperature Fast Flow Reactor,⁽¹⁾ the global formation rate for NO will be determined for the reactions 3.1 - 3.3, using resonance fluorescence to detect the NO. The resonance lamp contains a 2:1:1 mixture of He:N₂O:N₂ at 1-5 Torr within a 100 W microwave discharge. The light is imaged into flow tube center and fluorescence collected by a Hamamatsu R763P photomultiplier wired for photon counting. An interference filter rejects all light except emission from the A²Σ⁺(v=1) → X²Π(v=0) band of NO at 2150 Å. A preliminary sensitivity of ~ 1.3 x 10¹⁰ molecules cm⁻³ with a S/N = 1 in 10 seconds of counting has been determined. This is adequate to determine any NO product channels which are >1% of the total reaction rate.

The sources for NH₃ and SO₂ are straightforward, since these are stable, pure gases. NH₂ is prepared by reacting excess NH₃ with F atoms.⁽²⁾ The

formation of NH is more difficult and we will concentrate on obtaining a clean source of these radicals. This may be possible by reacting metastable Ar formed in a microwave discharge with NH_3 .

3.3 Work Forecast

During the next quarter, the global NO formation rate constants from the $\text{NH}_1 + \text{SO}_2$ reactions will be measured over the temperature range 300 - 1200 K.

4. SULFUR-BEARING SPECIES RATE COMPILATION

4.1 Task Goals and Milestones

The goals of this task are to evaluate the reactions and species which may be important in the reduction of NO emissions in combustor exhaust gases containing sulfur-bearing compounds such as COS and SO₂. During this quarter, a comprehensive search and compilation of measured and theoretical reaction rates of sulfur species has been completed. We have now begun to evaluate this information, as well as identify reactions for which no data exists but may well be of importance.

4.2 Rate Compilation

Using computer searches as well as some recent reviews, a list of reaction rates has been compiled. These reactions involve the species S, S₂, HS, H₂S, CS, CS₂, COS, NS, HSO, HSO₂, H₂SO₄, SO, SO₂, S₂O, and SO₃. Using the more recent critical evaluation reviews as a guide, we present the complete reaction list in Table 1, giving only what we presently feel is the best rate constant in the 1000 - 1500 K temperature range. Experimental results are always preferred over theoretical values. At this point, we have only begun to evaluate which reactions are important to the NH_i/NO_x/SO_x system. The reactions which are eventually selected will be added to our basic NH_i/NO_x reaction set.⁽²⁴⁾

In assessing this list, it is apparent that virtually no information of reactions between sulfur- and nitrogen-containing species exists. It seems that the reactions listed below are of possible importance and bear further evaluation. Note that the first reaction is that identified in Task 1.

TABLE 1 - LIST OF SULFUR REACTIONS HAVING POSSIBLE
 RELEVANCE TO $\text{NH}_3/\text{NO}_x/\text{SO}_x$ CHEMISTRY
 RATE ($k = AT^n \exp(-E/RT) (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$)

REACTION	A	n	E/R	REF.
$\text{S} + \text{HS} \rightarrow \text{H} + \text{S}_2$	1.0 - 10	0	0	3
$\text{H} + \text{HS} \rightarrow \text{S} + \text{H}_2$	2.5 - 11	0	0	4
$\text{H} + \text{H}_2\text{S} \rightarrow \text{HS} + \text{H}_2$	1.29 - 11	0	860	4
$2 \text{HS} \rightarrow \text{H}_2\text{S} + \text{S}$	1.3 - 11	0	860	4
$\rightarrow \text{H}_2 + \text{S}_2$	Unimportant			4
$\text{OH} + \text{H}_2\text{S} \rightarrow \text{HS} + \text{H}_2\text{O}$	1.1 - 11	0	225	5
$\text{SO} + \text{OH} \rightarrow \text{H} + \text{SO}_2$	9.67 - 11	0	0	5
$\text{HS} + \text{O}_2 \rightarrow \text{SO} + \text{OH}$	1.0 - 13	0	0	5
$\text{S} + \text{OH} \rightarrow \text{SO} + \text{H}$	6.7 - 11	0	0	6
$\rightarrow \text{HS} + \text{O}$	2.2 - 12	0.5	12700	7
$\text{O} + \text{HS} \rightarrow \text{SO} + \text{H}$	3.8 - 13	0.67	960	4
$\text{O} + \text{H}_2\text{S} \rightarrow \text{HS} + \text{OH}$	7.2 - 12	0	1660	5
$\rightarrow \text{SO} + \text{H}_2$	Unimportant			5
$\text{S} + \text{H}_2\text{O} \rightarrow \text{HS} + \text{OH}$	7.2 - 12	0	19000	3
$\text{S} + \text{O}_2 \rightarrow \text{SO} + \text{O}$	1.7 - 11	0	2820	5
$\text{O} + \text{S}_2 \rightarrow \text{SO} + \text{S}$	6.7 - 12	0	0	4
$\text{SO} + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}$	6.0 - 13	0	3300	5
$\text{S} + \text{SO}_2 \rightarrow 2 \text{SO}$	1.7 - 13	0	0	4
$\text{O} + \text{S}_2\text{O} \rightarrow 2 \text{SO}$	1.5 - 12	0	0	8
$\text{HO}_2 + \text{SO}_2 \rightarrow \text{SO}_3 + \text{OH}$	1.0 - 18	0	0	5
$\text{H} + \text{HSO}_2 \rightarrow \text{H}_2 + \text{SO}_2$	5.0 - 12	0	0	4
$\text{OH} + \text{HSO}_2 \rightarrow \text{H}_2\text{O} + \text{SO}_2$	8.0 - 12	0	0	4
$\text{S} + \text{SO}_3 \rightarrow \text{SO} + \text{SO}_2$	<7 - 12	0	0	3
$\text{SO} + \text{SO}_3 \rightarrow 2 \text{SO}_2$	<7 - 12	0	0	3
$\text{H} + \text{SO}_3 \rightarrow \text{OH} + \text{SO}_2$	2.0 - 15	0	0	9
$\text{O} + \text{SO}_3 \rightarrow \text{O}_2 + \text{SO}_2$	2.5 - 13	0	0	10
$\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{Products}$	9.1 - 13	0	0	11
$\text{O}_3 + \text{SO}_2 \rightarrow \text{O}_2 + \text{SO}_3$	No Reaction			
$\text{O}_3 + \text{S} \rightarrow \text{O}_2 + \text{SO}$	1.2 - 11	0	0	5
$\text{O}_3 + \text{SO} \rightarrow \text{SO}_2 + \text{O}_2$	2.5 - 11	0	1100	5
$\text{O}_3 + \text{H}_2\text{S} \rightarrow \text{SO}_2 + \text{H}_2\text{O}$	Unknown	0	0	4
$\text{O} + \text{CS} \rightarrow \text{CO} + \text{S}$	2.7 - 10	0	760	5
$\text{CS} + \text{O}_2 \rightarrow \text{COS} + \text{O}$	1.0 - 18	0	0	5
$\rightarrow \text{CO} + \text{SO}$				
$\text{O} + \text{COS} \rightarrow \text{CO} + \text{SO}$	2.6 - 11	0	2250	5
$\rightarrow \text{CO}_2 + \text{S}$	6.8 - 11	0	2250	5
$\text{O} + \text{CS}_2 \rightarrow \text{CS} + \text{SO}$	5.8 - 11	0	700	5
$\rightarrow \text{CO} + \text{S}_2$	3.2 - 12	0	520	5
$\rightarrow \text{COS} + \text{S}$	1.18 - 16	0	1040	4

TABLE 4 (Cont.)

<u>REACTION</u>		<u>A</u>	<u>n</u>	<u>E/R</u>	<u>REF.</u>
COS + S	→ CO + S ₂	2.8 - 12	0	2050	4
	→ CS + SO	No Reaction			4
	→ CS + O	No Reaction			4
CS + SO	→ CO + S ₂	1.7 - 15			4
COS + PH	→ Products	5.6 - 14	0	0	12
CS ₂ + OH	→ Products	<1.9 - 13	0	0	12
CS ₂ + O ₂	→ CS + SO ₂	1.67 - 12	0	2200	4
CS ₂ + SO	→ S ₂ + COS	4.3 - 17	0	100	4
CS ₂ + S	→ S ₂ + CS	1.67 - 10	0	2050	4
COS + SO	→ CO ₂ + S ₂	1.7 - 13	0	0	4
	→ CO + S ₂ O	No Reaction			4
COS + H	→ CO + HS	1.52 - 11	0	1950	4
NO ₂ + SO	→ SO ₂ + NO	1.36 - 11	0	0	13
NO ₂ + SO ₂	→ SO ₃ + NO	1.05 - 11	0	13590	14
NO ₂ + SO ₃	→ SO ₂ + NO + O ₂	2.7 - 11	0	13590	15
NO ₂ + S	→ SO + NO	5.0 - 11	0	-84	16
N + COS	→ CO + NS	3.3 - 13	0	0	4
N + SO ₃	→ SO ₂ + NO	<5.0 - 16	0	0	4
N + SO	→ NO + S	8.0 - 13	0	0	4
NO + HS	→ Products	6.3 - 13	0	0	4
CN + COS	→ SCN + CO	7.3 - 11	0	0	17
NOS + S	→ S ₂ + NO	Unknown			4
S + NO	→ SO + N	6.7 - 13	0.5	17260	7
	→ SN + O	1.7 - 12	0.5	17365	7
N + SO	→ SN + O	2.6 - 12	0.5	8250	7
S + NH	→ SN + H	1.1 - 12	0.5	0	7
	→ HS + N	1.1 - 12	0.5	4025	7
N + HS	→ SN + H	1.1 - 12	0.5	402	7
S + CN	→ CS + N	1.1 - 12	0.5	0	7
N + SN	→ N ₂ + S	1.1 - 12	0.5	0	7
2 S	M → S ₂	1.5 - 34	0	-900	3
	M → SO	1.5 - 34	0	-900	3
S + O	M → HS	20 - 32	0	0	3
H + S	M → H ₂ S	3.0 - 33	0	0	18
O + SO	M → SO ₂	2.4 - 26	-1.8	0	19
O + SO ₂	M → SO ₃	1.48 - 19	-3.75	0	5
H + SO ₂	M → HSO ₂	1.4 - 32	0	0	4
OH + SO ₂	M → HSO ₃	4.58 - 24	-2.9	0	5

TABLE 4 (Cont.)

<u>REACTION</u>		<u>A</u>	<u>n</u>	<u>E/R</u>	<u>REF.</u>
$\text{HO}_2 + \text{SO}_2$	$\xrightarrow{\text{M}} \text{HO}_2 \text{ SO}_2$	<4.2 - 31	0	0	20
$\text{O}_2 + \text{SO}$	$\xrightarrow{\text{M}} \text{SO}_3$	Unknown			
$\text{O} + \text{SO}_3$	$\xrightarrow{\text{M}} \text{SO}_2 + \text{O}_2$	2.0 - 31	0	-785	21
2S_2	$\xrightarrow{\text{M}} \text{S}_4$	1.4 - 31	0	0	4
$\text{S} + \text{NO}$	$\xrightarrow{\text{M}} \text{SNO}$	5.3 - 31	0	0	22
$\text{SO}_2 + \text{CO}$	$\xrightarrow{\text{M}} \text{Products}$	No Recommendation	0	0	23
$\text{S} + \text{COS}$	$\xrightarrow{\text{M}} \text{COS}_2$	8.3 - 33	0	0	4
$\text{S} + \text{CO}$	$\xrightarrow{\text{M}} \text{COS}$	5.56 - 32	0	910	4
CS_2	$\xrightarrow{\text{M}} \text{CS} + \text{S}$	4.3 - 9	0	38960	4
$\text{CS}_2 + \text{S}$	$\xrightarrow{\text{M}} \text{CS}_3$	8.3 - 31	0	0	4

4.3 Work Forecast

During the next quarter, the list of sulfur reactions will be evaluated and the key reactions identified will be incorporated into the rate package. Any newly published results will be added to the list. In addition, key reactions for which no data exists will be identified and, if possible, measured in our flow reactor.

5. REFERENCES

1. M.E. Gersh, J.A. Silver, M.S. Zahniser, C.E. Kolb, R.G. Brown, C.M. Gozewski, S. Kallelis, and J.C. Wormhoudt, "A Versatile High Temperature Flow Reactor for Kinetic and Spectroscopic Studies," (in preparation).
2. W. Hack, H. Schacke, M. Schroter, and H. Wagner, 17th Symp.(Int.) on Combustion, The Combustion Institute, p. 505 (1979).
3. C.H. Muller III, K. Schofield, M. Steinberg, and H.P. Broida, 17th Symp. (Int.) on Combustion, 867 (1978).
4. D.L. Baulch, D.D. Drysdale, J. Duxbury, and S. Grant, Evaluated Kinetic Data for High Temperature Reactions, Vol. 3, Butterworth (London, 1976)
5. D.L. Baulch, R.A. Cox, R.F. Hampson, Jr., J.A. Kerr, J. Troe, R.T. Watson, J. Phys. Chem. Ref. Data 9, 295 (1980).
6. J.L. Jourdain, Int. J. Chem. Kin. 11 509 (1979).
7. S.W. Benson, D.M. Golden, R.W. Lawrence, R. Shaw and R.W. Woolfolk, EPA Report No. EPA-600/2-75-019 (1975).
8. D.H. Stedman, J. Phys. Chem. 78, 1248 (1974).
9. K. Chung, H. Alvord, and A. Baker-Blocker, Int. J. Chem. Kin. 7, 161 (1975).
10. E.L. Merryman, J.G. Calvert, and J.W. Bottenhelm, 17th Symp. (Int.) on Combustion, 727 (1979).
11. A.W. Castleman, Jr., and A. Levy, Int. J. Chem. Kin. Symp. 1, 629 (1975).
12. R.E. Davis, H.R. Munkelwitz, I.N. Tang, and W.P. Wood, Chemical Kinetic and Photochemical Data for Use in Stratospheric Modeling NASA Panel for Data Evaluation, JPL Publication 79-27, Jet Propulsion Laboratory (1979).
13. M.S. Clyne and A.J. Macrobert, Int. J. Chem. Kin. 12, 79 (1980).
14. J.W. Armitage and C.F. Cullis, Comb. Flame 16, 125 (1971).
15. C.F. Cullis and M.F.R. Mulcahy, Comb. Flame 18, 225 (1972).
16. M.A. Clyne and P.D. Whitefield, J. Chem. Soc. Far Trans. II 75, 1327 (1979).
17. M.C. Addison, A.J. Leitch, C. Fotakis, and R.J. Donovan, J. Photochem. 10, 373 (1979).
18. C.T. Bowman and L.G. Dodge, 16th Symp. (Int.) on Combustion, 971 (1977).

REFERENCES (Cont.)

19. Kiefer, J. Chem. Phys. 62, 1354 (1975).
20. Burroughs, Proc. Roy Soc. (London) A368, 463 (1979).
21. Westenberg, DeHaas, J. Chem. Phys. 63, 5411 (1975).
22. VanRoodselaar, Int. J. Chem. Kin. 10, 31 (1978).
23. F. Westley, NBSIR 80-2118 (1980).
24. J.A. Silver, C.M. Gozewski, and C.E. Kolb, "The Homogeneous Chemistry of NO_x Production and Removal from Fossil Fuel Combustion Gases," Aerodyne Research, Inc. Report No. ARI-RR-235 (1980).