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Ammonia oxidation at high pressure and intermediate temperatures

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ABSTRACT

Ammonia oxidation experiments were conducted at high pressure (30 bar and 100 bar) under oxidizing and stoichiometric conditions, respectively, and temperatures ranging from 450 to 925 K. The oxidation of ammonia was slow under stoichiometric conditions in the temperature range investigated. Under oxidizing conditions the onset temperature for reaction was 850–875 K at 30 bar, while at 100 bar it was about 800 K, with complete consumption of NH_3 at 875 K. The products of reaction were N_2 and N_2O, while NO and NO_2 concentrations were below the detection limit even under oxidizing conditions. The data were interpreted in terms of a detailed chemical kinetic model. The rate constant for the reaction of the important intermediate H_2NO with O_2 was determined from ab initio calculations to be $2.3 \times 10^2\ T^{2.994} \exp(-9510\ \mathrm{K}/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$. The agreement between experimental results and model work was satisfactory. The main oxidation path for NH_3 at high pressure under oxidizing conditions is $NH_3 \xrightarrow{+OH} NH_2 \xrightarrow{+HO_2,NO_2} H_2NO \xrightarrow{+O_2} HNO \xrightarrow{+O_2} NO \xrightarrow{+NH_2} N_2$. The modeling predictions are most sensitive to the reactions $NH_2 + NO = NNH + OH$ and $NH_2 + HO_2 = H_2NO + OH$, which promote the ammonia consumption by forming OH radicals, and to $NH_2 + NO = N_2 + H_2O$ and $NH_2 + NO_2 = N_2O + H_2O$, which are the main chain-terminating steps.

1. Introduction

Ammonia is an important combustion intermediate in formation of nitric oxide from nitrogen organically bound in fuels. For most solid fuels, NH_3 is formed directly during devolatilization [1], and it has also been reported as a product of gasification [2]. The selectivity for forming NO or N_2 from N-volatiles in combustion depends largely on the fate of amine radicals such as NH_2, NH, and N [1,3]. Ammonia is also known as an efficient additive for Selective Non-Catalytic Reduction of NO (SNCR) [3,4]. Recently, ammonia has attracted interest as a potential carbon-free energy carrier [5]. Results on oxidation of NH_3 are available from flames [6–16], shock tubes [17–27], and flow reactors [2,28–30]. In addition, a number of modeling studies and reviews of ammonia chemistry have been reported [3,27,28,31–35]. Supplementing the oxidation studies, extensive work has been conducted on the kinetics of the SNCR process [3,4,36–38].

With the interest in amine-based fuels as energy carriers [39], reliable experimental data for oxidation of ammonia at high pressure become important. High-temperature results at increased pressure are available from recent work in shock tubes and premixed flames. Mathieu and Petersen [27] measured the ignition time for ammonia diluted in Ar at 1.4, 11, and 30 bar, respectively, while Hayakawa et al. [15] determined the burning velocity of ammonia/air mixtures at pressures of 1–5 bar. However, studies of ammonia oxidation at low-to-medium temperatures and high pressure are scarce.

The purpose of the present study is to investigate ammonia oxidation at high pressure (30–100 bar) and temperatures up to 925 K. Experiments are conducted with stoichiometric and lean NH_3/O_2 mixtures, highly diluted in N_2, in a laminar flow reactor. The results are interpreted in terms of a detailed chemical kinetic model for ammonia oxidation. The reaction mechanism, which is based on earlier work on nitrogen chemistry [34,38,40,41], is updated in the present work, emphasizing reactions important at high pressure. Under the present conditions, the nitroxide radical H_2NO is an important intermediate, and the rate constant for the

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reaction between H_2NO and O_2 has been derived from ab initio calculations.

2. Experimental

The experimental setup was a laboratory-scale high-pressure laminar flow reactor designed to approximate plug flow. The setup is described in detail elsewhere [42] and only a brief description is provided here. The system was used here for investigation of ammonia oxidation at 30 bar and 100 bar pressure, respectively, and temperatures from 450 to 925 K. The reactant gases were premixed before entering the reactor. The reactions took place in a tube under laminar flow conditions. The tube was made of quartz (inner diameter of 7.5 mm) or alumina (Degussit AL23, inner diameter 6 mm). The temperature profile in the flow reactor was measured by a thermocouple positioned in the void between the quartz reactor and the steel shell. Results for 100 bar are shown in Fig. 1 while the 30 bar profiles are available as supplementary material. An isothermal reaction zone of 39–47 cm was achieved in the reactor. All gases used in the present experiments were high purity gases or mixtures with certified concentrations. The total flow rate was 2.8 L min^{-1} (STP). The product analysis was conducted with an on-line 6890N Agilent Gas Chromatograph (GC-TCD/FID from Agilent Technologies) and an AO2020 $NH_3/NO/NO_2$ analyser from ABB. The relative measurement uncertainties for the species detected were in the range ±2–6%.

3. Chemical kinetic model

The starting mechanism and corresponding thermodynamic properties were drawn from the recent work by Klippenstein et al. [38]. The mechanism was carefully updated, emphasizing reactions of importance under the conditions of the present study. Table 1 lists the key reactions in the NH_3 oxidation scheme with the rate coefficients used in the present work. The full mechanism is available as supplemental material.

At the high-pressure medium-temperature conditions of this work, ammonia oxidation occurs to a significant extent through the H_2NO intermediate. Rate constants for H_2NO reactions are generally quite uncertain. In the present work, we characterize the key reaction of H_2NO with O_2 by ab initio calculations, as described below.

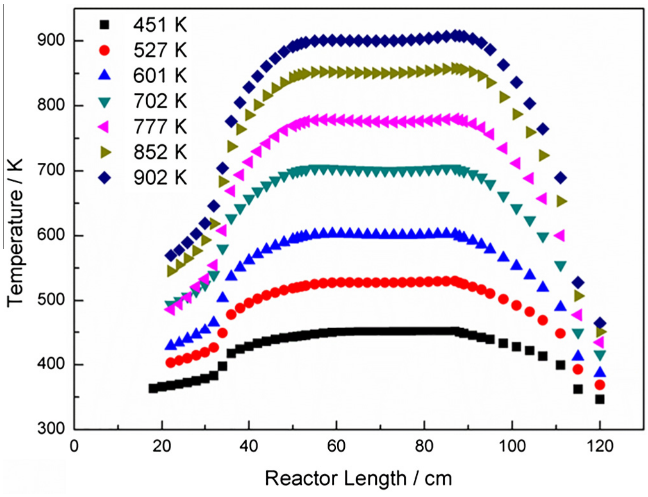

Fig. 1. Measured temperature profiles along the reactor axis for 100 bar conditions.

Table 1
Selected reactions from the NH_3 subset. Parameters for use in the modified Arrhenius expression $k = AT^{\beta} \exp(-E/[RT])$. Units are mol, cm, s, cal.

		A	β	E	Source
1	$NH_2 + H(+M) \rightleftharpoons NH_3(+M)$	1.6E14	0.000	0	[43]
	Low pressure limit:	3.6E22	−1.760	0	
	Troe parameters: 0.5 1.0E−30 1.0E30				
2	$NH_3 + H \rightleftharpoons NH_2 + H_2$	6.4E05	2.390	10,171	[44]
3	$NH_3 + O \rightleftharpoons NH_2 + OH$	9.4E06	1.940	6460	[45]
4	$NH_3 + OH \rightleftharpoons NH_2 + H_2O$	2.0E06	2.040	566	[46]
5	$NH_3 + HO_2 \rightleftharpoons NH_2 + H_2O_2$	3.0E11	0.000	22,000	[3] est
6	$NH_2 + HO_2 \rightleftharpoons NH_3 + O_2$	1.7E04	1.550	2027	[47][a]
7	$NH_2 + H \rightleftharpoons NH_2 + H_2$	7.2E05	2.320	799	[48]
8	$NH_2 + O \rightleftharpoons HNO + H$	6.6E13	0.000	0	See [41]
9	$NH_2 + O \rightleftharpoons NH + OH$	7.0E12	0.000	0	See [41]
		8.6E−1	4.010	1673	
10	$NH_2 + OH \rightleftharpoons NH + H_2O$	3.3E06	1.949	−217	[38,49]
11	$NH2 + HO_2 \rightleftharpoons H_2NO + OH$	5.0E13	0.000	0	See text
12	$NH_2 + HO_2 \rightleftharpoons HNO + H_2O$	1.6E07	0.550	525	[47][a,b]
		5.7E15	−1.120	707	
13	$NH_2 + HO_2 \rightleftharpoons HON + H_2O$	2.1E07	0.640	811	[47][a]
14	$NH_2 + O_2 \rightleftharpoons H_2NO + O$	2.6E11	0.487	29,050	[38]
15	$NH_2 + O_2 \rightleftharpoons HNO + OH$	2.9E−2	3.764	18,185	[38]
16	$NH_2 + NH_2 \rightleftharpoons NH_3 + NH$	5.6E00	3.530	552	[49]
17	$NH_2 + HNO \rightleftharpoons NH_3 + NO$	3.6E06	1.630	−1250	[50]
18	$NH_2 + NO \rightleftharpoons N_2 + H_2O$	1.3E16	−1.25	0	[38]
		−3.1E13	−0.48	1180	
19	$NH_2 + NO \rightleftharpoons NNH + OH$	3.1E13	−0.48	1180	[38]
20	$NH_2 + NO_2 \rightleftharpoons N_2O + H_2O$	2.6E18	−2.191	455	[51]
21	$NH_2 + NO_2 \rightleftharpoons H_2NO + NO$	9.1E11	0.032	−1512	[51]
22	$NH_2 + HONO \rightleftharpoons NH_3 + NO_2$	7.1E01	3.020	−4940	[50]
23	$H_2NO + M \rightleftharpoons HNO + H + M$	2.8E24	−2.830	64,915	[33]
24	$H_2NO + H \rightleftharpoons HNO + H_2$	3.0E07	2.000	2000	[36] est
25	$H_2NO + H \rightleftharpoons NH_2 + OH$	5.0E13	0.000	0	[36] est
26	$H_2NO + O \rightleftharpoons HNO + OH$	3.0E07	2.000	2000	[36] est
27	$H_2NO + OH \rightleftharpoons HNO + H_2O$	1.0E14	0.000	0	[52]
28	$H_2NO + HO_2 \rightleftharpoons HNO + H_2O_2$	2.9E04	2.690	−1600	[33]
29	$H_2NO + O_2 \rightleftharpoons HNO + HO_2$	2.3E02	2.994	18,900	pw
30	$H_2NO + NH_2 \rightleftharpoons HNO + NH_3$	3.0E12	0.000	1000	[36] est
31	$H_2NO + NO_2 \rightleftharpoons HONO + HNO$	6.0E11	0.000	2000	[53] est
32	$HNO + O_2 \rightleftharpoons NO + HO_2$	2.0E13	0.000	16,000	[33]
33	$NNH \rightleftharpoons N_2 + H$	1.0E09	0.000	0	[38]
34	$NNH + O_2 \rightleftharpoons N_2 + HO_2$	5.6E14	−0.385	−13	[38]

[a] Rate constant calculated for 1 atm.
[b] Duplicate reaction – the resulting rate constant is the sum of the two expressions.

3.1. Ab initio calculations

The nitroxide radical H_2NO, molecular oxygen and the transition state for their reaction were investigated computationally. First, geometries and frequencies (scaled by a standard factor of 0.954 [54]) were obtained with UQCISD/6-311G(d,p) theory, using spin-unrestricted wavefunctions as implemented within the Gaussian 09 code [55]. At these geometries (see Fig. 2), single-point energies were calculated at the UCCSD(T) level of theory with the aug-cc-pVTZ and aug-cc-pVQZ basis sets, using spin-restricted wavefunctions within the Molpro 2010 program [56], and extrapolated to the complete basis set limit for coupled cluster theory (CCSD(T)/CBS). Corrections were added to this result based on UCCSD(T)/cc-pwVTZ results obtained with core electrons included and excluded from the correlation treatment, and relativistic effects evaluated at the CISD/cc-pwVTZ level of theory. The results are summarized in the supplementary material. The rate constant was then derived via canonical transition state theory as implemented within the Multiwell program suite [57], with tunneling accounted for via the Eckart model.

Some of the prior studies of H_2NO raised the issue of whether this molecule is planar or pyramidal [58,59]. Out-of-plane bending