

A Study of Rich Ammonia/Oxygen/Nitrogen Flames

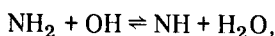
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NH₃, NH₂, NH, OH and temperature measurements in the flame gases of three rich NH₃/O₂/N₂ flames are reported. The equilibration of NH₂ and NH with NH₃ via reactions with OH and H is confirmed and a value for the *f* number of the NH₂ rotational line at 5166 Å is determined. The decay of the greater than equilibrium concentrations of the NH_i species (NH_i = NH₃, NH₂ and NH) and the net dissociation rates observed are discussed.

INTRODUCTION

In recent years there has been much interest in the fate of fuel nitrogen in combustion processes. To this end the combustion of ammonia in oxygen has been studied in flames [1, 2] and flame gases [3, 4, 5, 6]. Nadler et al. [3] showed that the flame gases of rich NH₃/O₂/N₂ flames are characterized by OH concentrations near calculated equilibrium values and NH₂ and NH concentrations very much greater than calculated equilibrium values. They also demonstrated that NH₂ and NH are equilibrated via the balanced reaction



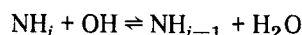
and they have determined a value for the line oscillator strength of the NH₂ ^RQ_{0,4} line in the (0, 12, 0)-(0, 0, 0) band at 5166 Å. They suggested a qualitative mechanism for the decay of radicals. In another study of similar flames, Kaskan and Nadler [4] demonstrated that the function

$$\frac{[\text{NH}][\text{H}_2\text{O}]^2}{[\text{NH}_3][\text{OH}]^2},$$

has the temperature dependence of an equilibrium constant and suggested a new value of Δ*H*_{*f*} for

NH. Kaskan and Hughes [5, 6] studied the flame gases of some lean NH₃/O₂ flames and verified the equilibration of NH and NH₃ and interpreted their data with a relatively complete mechanism. Some of their data and conclusions have recently been questioned by Fenimore [7].

This paper reports the study of the flame gases of three very rich (*φ* ≥ 1.5) NH₃/O₂/N₂ flames by spectroscopic methods. The equilibration of the NH_i species via reactions of the form



has been verified and a new value for the line oscillator strength (*f*_{*i*}) of the NH₂ ^RQ_{0,4} line is determined. The observed concentration profiles are examined with regards to the destruction of the NH_i species and to dissociation reactions in the flame gases. An approximate rate constant is deduced for the thermal dissociation of NH₃ in the presence of H₂O.

EXPERIMENTAL

For the most part the apparatus and experimental procedures have been described previously [3, 4]. Briefly, commercial gases are metered through critical flow orifices and fed at atmospheric pressure to a movable, shielded 5 × 9 cm flat flame burner situated in an optical system. A White

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TABLE 1

Flame No.	ϕ	Cold gas velocity (v_{25}) (cm sec ⁻¹)	NH ₃ /O ₂ /N ₂	T (K) (at. 7 mm)	$-(dT/dz)$ °K cm ⁻¹
1	1.5	13	1/.50/.25	2083	81
2	1.7	11	1/.44/.22	1989	111
3	1.81	14	1/.41/.15	2018	108

multiple pass optical system was used in the OH, NH and NH₂ absorption experiments, providing approximately 1.5 mm spatial resolution and a 100 cm optical path length. A 5 cm path length was used in the NH₃ absorption experiments. The background source was a 1000 W high pressure Xe arc lamp. For the NH₃ work, a 0.25 meter monochromator was employed as a filter. Spectral intensity measurements were made with a SPEX model 1500 grating spectrometer equipped for photoelectric recording.

The NH₃ measurements were made at 2300 Å, a region assigned as a quasicontinuous hot band. The extinction coefficients of Menon and Michel [8] were used. This method has been calibrated previously [4, 6] in similar systems and the extinction coefficients were found to be reliable to within a factor of 1.5.

As in previous work [3, 4], OH, NH and NH₂ measurements were made using single rotational absorption lines. For OH the P_{15} line of the 0-0 band of the $^2\Sigma^+ \leftarrow ^2\Pi$ transition at 3101 Å, for NH the P_{37} line of the 0-0 band of the $^3\Pi \leftarrow ^3\Sigma^-$ transition at 3385 Å and for NH₂ the $R_{0,4}$ line of the (0, 12, 0) \leftarrow (0, 0, 0) band of the $A \leftarrow X$ transition at 5166 Å were employed. The curve of growth method was used to obtain [OH], [NH] and $f_i[\text{NH}_2]$ from absorption measurements. The molecular data required, i.e., the line oscillator strengths and broadening parameters, are available [3]. The oscillator strength of the NH₂ line used was taken to be unknown and a new value is deduced in the next section. Temperatures were determined by sodium reversal measurements.

Table 1 contains the essential data for the flames studied.

RESULTS AND DISCUSSION

Results

Concentration and temperature measurements were taken from 3 to 10 or 13 mm from the burner surface. These data for flames 1 and 3 are shown in Figs. 1 and 2. Uncertainties due to signal noise are estimated to range from about $\pm 5\%$ in the richer two flames near the burner surface to about $\pm 20\%$ in the leanest flame at large distances from

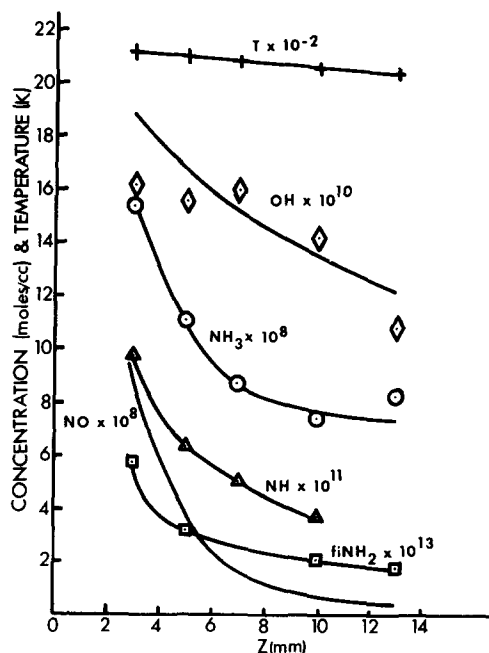


Fig. 1. Concentrations and temperature as a function of distance for flame 1 ($\phi = 1.5$). The NO curve is calculated (see text). The solid curves were used in the modeling procedures.

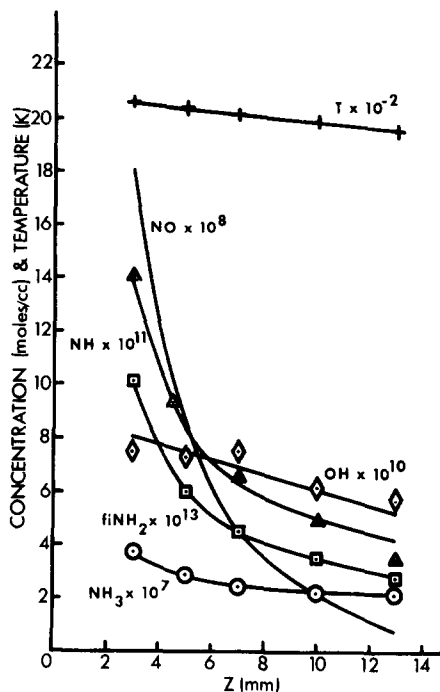


Fig. 2. Concentrations and temperature as a function of distance for flame 3 ($\phi = 1.81$).

the burner. The f_i used for NH and OH have been estimated to be accurate to about $\pm 10\%$. Temperature measurements are thought to be accurate to $\pm 15^\circ\text{K}$. The concentration and temperature profiles were fit to smooth curves and these curves were used in subsequent kinetic analysis. The temperature gradient is approximately constant throughout each flame.

The concentration profiles of the three flames share certain features. All the NH_i ($i = 1, 2, 3$) species decay in a parallel manner to values "constant" on the time scale of the experiments (msec). These final values are very much larger than calculated equilibrium values. For example, for flame 2 at 13 mm $[\text{NH}_3]/[\text{NH}_3]_{\text{eq}} = 2.7 \times 10^4$. OH also decays but more slowly and to values very close to calculated equilibrium values (*vide infra*).

Equilibration of the NH_i Species

There is considerable evidence that the NH_i species are equilibrated via reactions with OH and H in the

flame gases in both rich and lean ammonia flames.



It has been shown [3, 4] that the function F_1 and the product $F_1 \times F_2$

$$F_1 = \frac{[\text{NH}][\text{H}_2\text{O}]}{[\text{NH}_2][\text{OH}]}, \quad F_2 = \frac{[\text{NH}_2][\text{H}_2\text{O}]}{[\text{NH}_3][\text{OH}]},$$

parallel, within the limits of experimental uncertainty, the temperature dependence of the appropriate equilibrium constants as calculated from the JANAF tables [9]. The functions F_1/f_i and $f_i F_2$ for the data reported here are shown in Figs. 3 and 4.

If the assumption of equilibration is made, two uncertain quantities, the f_i of the NH_2 $RQ_{0,4}$ line and the ΔH_f of NH, can be simultaneously determined. Kaskan and Nadler [4] showed that $F_1 \times F_2$ in systems similar to those reported here cannot differ significantly from the corresponding equilibrium constant. They ascribed the difference of their experimental findings from the $K_1 \times K_2$ calculated from the JANAF tables to an error in the previously accepted value of the NH ΔH_f . They found that a value of 90.5 kcal/mole for this quantity best fits their data. Since then a value of 90 ± 4 kcal/mole has been proposed in an independent updating of the JANAF tables [10]. The

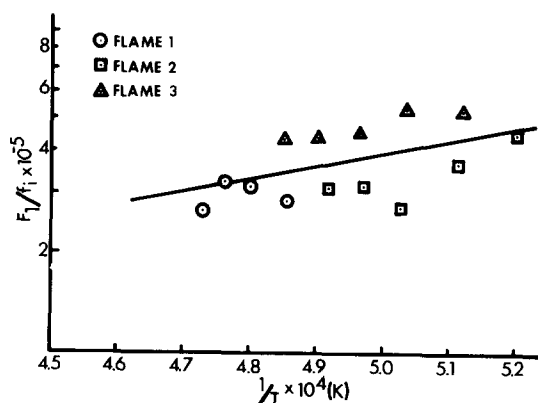


Fig. 3. $F_1/f_i(\text{NH} \cdot \text{H}_2\text{O}/\text{NH}_2 \cdot \text{OH})$ vs $1/T$. Line is calculated K_1/f_i from JANAF tables but with $\Delta H_f(\text{NH}) = 90.3$ kcal and $f_i = 2.4 \times 10^{-4}$.

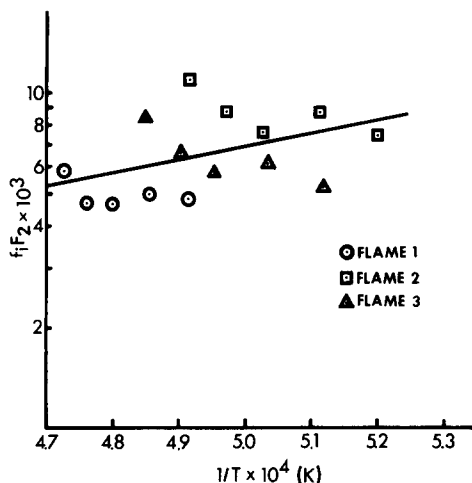


Fig. 4. $f_i F_2 / (f_i \text{NH}_2 \cdot \text{H}_2\text{O} / \text{NH}_3 \cdot \text{OH})$ vs $1/T$. Line is calculated $f_i K_2$ from JANAF tables and with $f_i = 2.4 \times 10^{-4}$.

results of this work concur. A value of 90.3 ± 3 kcal best fits the combined results of the three flames studied.

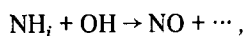
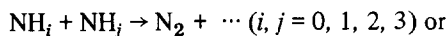
A value for the f_i of the NH_2 $RQ_{0,4}$ line is also deduced. Taking the value of the NH ΔH_f to be 90.3 kcal/mole, the value of f_i consistent with F_1/f_i , $f_i F_2$ and the tabulated thermochemical data [9, 10] is $2.4 \pm .8 \times 10^{-4}$. This value differs from the Nadler et al. value of 4×10^{-4} obtained in similar flames principally because of their use of older thermochemical data.

Destruction of the NH_i Species

The symbol $\Sigma[\text{NH}_i]$ is taken to be

$$\Sigma[\text{NH}_i] = [\text{NH}_3] + [\text{NH}_2] + [\text{NH}] + [\text{N}],$$

i.e., the total nitrogen concentration not yet in the form of N_2 or NO or other products. The fact that $\Sigma[\text{NH}_i] \approx 0$ when $\Sigma[\text{NH}_i]/\Sigma[\text{NH}_i]_{\text{eq}} \gg 1$ suggests that reactions of the form



cannot provide the principal path for the removal of $\Sigma[\text{NH}_i]$. This behavior of $\Sigma[\text{NH}_i]$ suggests a titration of one or several of the NH_i species with

a species outside the group, a species which largely disappears by the time $\Sigma[\text{NH}_i]$ nears zero. There is considerable evidence that suggests that NO is the species of interest. Fenimore and Jones [1] showed that in $\text{N}_2\text{O}/\text{H}_2/\text{NO}/\text{NH}_3$ flames $[\text{NH}_3]$ and $[\text{NO}]$ were approximately equal and that NO was stable in NH_3 free flames. MacLean and Wagner [2] showed in the post flame gases of a rich ($\phi = 1.39$) NH_3/O_2 flame NO and NH_3 both decayed after the O_2 was consumed. Nadler et al. [3] proposed an N-NO reaction as a principal path for N_2 formation in rich $\text{NH}_3/\text{O}_2/\text{N}_2$ flames. The Kaskan and Hughes [5, 6] mechanism for lean NH_3/O_2 flames includes NH and N reactions with NO for N_2 formation and Hughes [6] further indicates that these are the only significant paths for N_2 formation in those flames. In a NH_3/NO shock tube study, Duxbury and Pratt [11] also find that NH_3 and NO react stoichiometrically.

Preliminary modeling suggests that titration of the NH_i species with NO can explain the leveling off of the NH_i concentrations. Typical required NO profiles from this modeling are indicated in Figs. 1 and 2.

The modeling predicts a considerable quantity of NO in the upstream regions of these flames, but scans of the NO γ -band region detect no NO absorption. Although NH_3 absorption severely interferes in this spectral region, NO levels of the magnitude predicted by the modeling should be observable. The magnitude of NO concentrations and the role of NO in the kinetics of rich NH_3 flames remains an open question. NO concentration data determined in probe sampled gases should be used with caution. A recent study [12] indicates that probing in gases containing as little as .5% H_2 can destroy all NO_x .

Dissociation Reactions

It has been shown by Kaskan and Hughes [5, 6] in lean NH_3/O_2 flames that $[\text{OH}]$ is well below calculated equilibrium concentrations. They attribute this to the inability of the relatively slow dissociation reactions to keep up with radical-consuming reactions. This hypothesis is consistent with their observation that NH_3 flames cannot be stabilized at burned-gas temperatures less than about 1800°K.

Dissociation and recombination reactions in post flame gases are best analyzed within the framework of the Kaskan-Schott composition functions [13]. These functions allow the expression of the net rate of dissociation (or recombination) as a linear combination of the rates of change of the concentrations of some or all of the species present. These functions are mechanism-independent; i.e., once the identity of the species of the system is specified, the functions are dictated by stoichiometry.

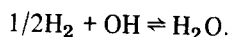
The following set of species was used in the construction of an appropriate concentration function, F_D : NH₃, NH₂, NH, N, N₂O, NO, HNO, H₂O, H₂, OH, H, O₂ and O. F_D is given by

$$F_D = -[\text{NH}_3] + [\text{O}_2] + [\text{O}] + 1/2([\text{NO}] + [\text{H}] + [\text{OH}] + [\text{N}] - [\text{NH}_2]).$$

The net rate of dissociation, R_D , is simply \dot{F}_D .

R_D is calculated using experimental [NH₃], [NH₂] and [OH], [NO] and [N] from the previously mentioned modeling and [H], [O] and [O₂] calculated assuming the equilibration of the O-H system. R_D is dominated by the [NH₃] and [NO] terms. R_D as a function of distance is plotted in Fig. 5. If the NO concentrations are much smaller than the modeling predicts and the [NO] term is negligible, R_D is approximately ($\pm 10\%$) twice as large as the plotted values.

In a system which is characterized by a net dissociation or recombination rate there must of necessity be unbalanced dissociation-recombination reactions. In systems such as the ones of this study, this imbalance can be characterized by the parameter, $\alpha = [\text{OH}]/[\text{OH}]_{\text{eq}}$, where $[\text{OH}]_{\text{eq}}$ is defined by the reaction:



This parameter, α , as a function of distance from the burner, is plotted in Fig. 6 for flame 3. The apparent overshoot of $\alpha = 1$ in the latter stage is thought to be a result of indeterminate experimental error.

H₂O, H₂, NH₃ and HNO were considered as possible contributors to R_D . H₂O, H₂ and NH₃

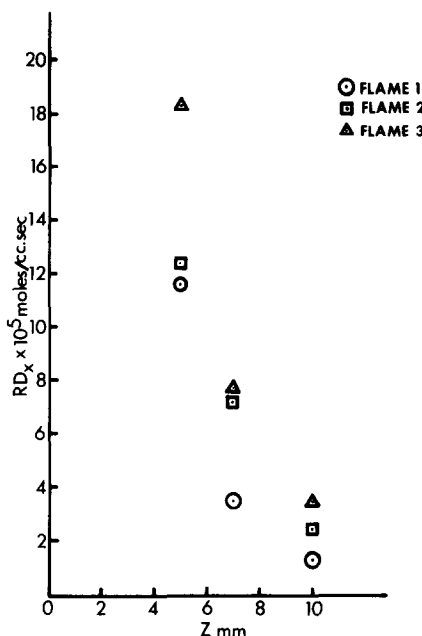


Fig. 5. Experimental R_D as a function of distance from burner.

were included because they are the major constituents with bond energies less than 125 kcal/mole and HNO was included despite a very small steady state concentration ($\sim 8 \times 10^{-12}$ mole cc⁻¹) because of the unusually small HNO bond energy (52.7 kcal/mole). HNO has been shown to be the intermediate in the NO catalysis of recombination in rich H₂ flames [14]. If the O-H and N-H systems are assumed to be equilibrated and the steady state approximation is used for [HNO], R_{Dc} , the calculated R_D , is given by:

$$R_{Dc} = R_{Dc}[\text{H}_2\text{O}] + R_{Dc}[\text{H}_2] + R_{Dc}[\text{NH}_3] + R_{Dc}[\text{HNO}],$$

where

$$R_{Dc}[\text{H}_2\text{O}] = k_1[\text{H}_2\text{O}][M](1 - \alpha^2)$$

$$R_{Dc}[\text{H}_2] = k_2[\text{H}_2][M](1 - \alpha^2)$$

$$R_{Dc}[\text{NH}_3] = k_3[\text{NH}_3][M](1 - \alpha^2)$$

$$R_{Dc}[\text{HNO}] = k_4[\text{HNO}]_{ss}[M] + k_{-4}[\text{H}][\text{NO}][M]$$

$$[\text{HNO}]_{ss} = \frac{(k_{-4}[\text{H}][\text{NO}][M] + k_5[\text{NH}_3][\text{NO}])}{(k_4[M] + k_{-5}[\text{NH}_2])}.$$

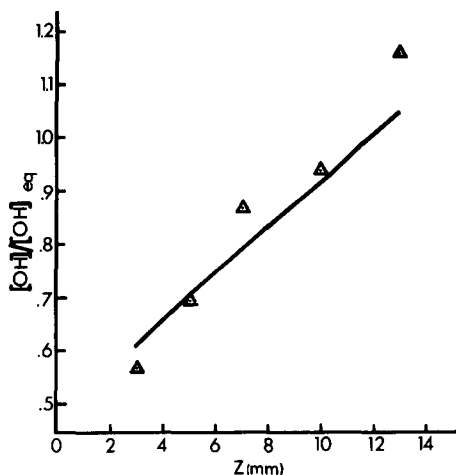


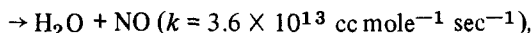
Fig. 6. $\alpha([\text{OH}]/[\text{OH}]_{\text{eq}})$ as a function of distance for flame 3 ($\phi = 1.81$). Line is calculated with smoothed OH data.

The rate constants k_1 through k_5 refer to the following reactions:

1. $\text{H}_2\text{O} + M \rightleftharpoons \text{H} + \text{OH} + M$
2. $\text{H}_2 + M \rightleftharpoons 2\text{H} + M$
3. $\text{NH}_3 + M \rightleftharpoons \text{NH}_2 + \text{H} + M$
4. $\text{HNO} + M \rightleftharpoons \text{H} + \text{NO} + M$
5. $\text{NH}_3 + \text{NO} \rightleftharpoons \text{NH}_2 + \text{HNO}$

Reactions 1 and 2 are well studied [15]. The rate constant k_4 was thermodynamically calculated from k_{-4} [16]. It is assumed that reactions 4 and 5 are the only important reactions influencing [HNO]. There are no literature values for k_5 or k_{-5} so k_{-5} was approximated by the literature value [16] of the rate constant for the reaction:

$\text{OH} + \text{HNO}$



and the forward rate constant was thermodynamically calculated. It was found that R_{Dc} was insensitive to this parameter, $R_{Dc}(\text{HNO})$ being on the order of 10–15% of the total R_{Dc} .

The rate of thermal dissociation of NH_3 at high temperatures has been determined in Ar [16]. The

relative third body efficiency of H_2O , however, has not. If $R_{Dc}[\text{H}_2\text{O}]$, $R_{Dc}[\text{H}_2]$ and $R_{Dc}[\text{HNO}]$ are subtracted from R_D , a value of k_3 can be determined. These apparent k_3 's are plotted in Fig. 7. It is found that NH_3 is the dominant dissociating species, accounting for about 70% of the dissociation in flame 1 and about 85% in flames 2 and 3. If the literature activation energy for Reaction 3 is used, the average third body efficiency is found to be approximately 1.8 times larger than the reported Ar efficiency. If it is assumed that the N_2 and H_2 third body efficiencies are equal to that of Ar the H_2O third body efficiency is found to be approximately 2.9. The results can be represented as:

$$k_3 = 2.7 \times 10^{16} \exp(-84.26 \text{ kcal}/RT)$$

$$M = \text{H}_2\text{O} \quad T \sim 1950\text{--}2100^\circ\text{K}.$$

If NO is ignored and hence the HNO contribution to R_{Dc} , the same considerations yield an average third body efficiency of 4.4 and an H_2O third body efficiency of about 9.5. This is a rather large value and might be taken as an indication that [NO] is not negligible. In any event reliable NO profiles would greatly aid in the kinetic analysis of these flames.

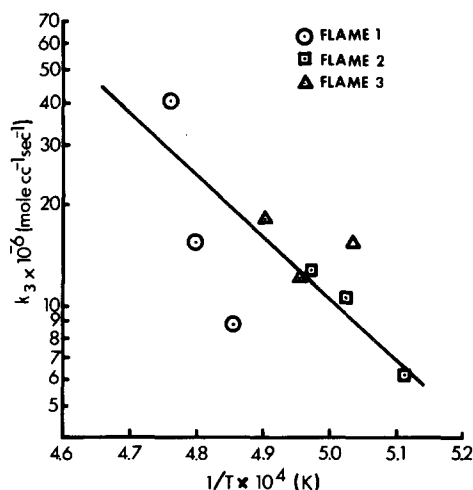


Fig. 7. Apparent k_3 with $[M] = [\text{H}_2\text{O}] + [\text{N}_2] + [\text{H}_2]$. The line represents an average third body efficiency of 1.8 relative to Ar.

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