Reaction between Nitric Oxide and Ammonia on Polycrystalline Platinum. 1. **Steady-State Kinetics**

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The reaction between nitric oxide and ammonia has been studied over polycrystalline platinum wires in a flow reactor at pressures between 0.2 and 1.0 torr, temperatures between 200 and 1200 °C, and feed compositions between $P_{\rm NO}/P_{\rm NH_3} = 1$ and 9. Partial pressures were monitored by a differentially pumped mass spectrometer. The only products observed below 850 °C are N₂, N₂O, and H₂O. The rate is proportional to $P_{NO}^{-1}P_{NH_3}^{1/2}$ and to $P_{\rm NO}P_{\rm NH_3}^{1/2}$ at low and high temperature limits, respectively. Data can be fitted quantitatively (within 15% at all temperatures, pressures, and compositions) by a single Langmuir-Hinshelwood (LH) rate expression. Arrhenius plots at low and high temperatures and pressures were used to obtain heats of adsorption and reaction activation energies. The proposed rate expression appears to fit all steady-state rate data on this reaction on Pt between 10^{-8} and 10^{-3} torr between 400 and 1500 K.

Introduction

The reduction of nitric oxide by ammonia is an important reaction for removing NO from gas streams.¹⁻⁵ This reaction also occurs in the removal of NO in the automotive catalytic converter and it is the undesired side reaction in HNO₃ synthesis.⁶

The two overall chemical reactions which describe the reaction between NO and NH₃ are

$$4\mathrm{NH}_3 + 6\mathrm{NO} \rightarrow 5\mathrm{N}_2 + 6\mathrm{H}_2\mathrm{O} \tag{1}$$

$$2\mathrm{NH}_3 + 8\mathrm{NO} \rightarrow 5\mathrm{N}_2\mathrm{O} + 3\mathrm{H}_2\mathrm{O} \tag{2}$$

and both are exothermic with favorable equilibrium constants. The kinetics of this reaction system has been studied over supported platinum catalysts at atmospheric pressure between 150 and 200 °C^{1,7-9} and over a stepped platinum single crystal at pressures on the order of 10^{-8} torr between 100 and 550 °C.¹⁰ Both research groups that worked over supported platinum catalysts observed N₂O and N₂ products and fitted their kinetic data with a rate law derived from their proposed mechanism.^{1,9} The other group¹⁰ observed only N₂ as a product, carried out temperature-programmed desorption and Auger electron spectroscopy studies, and proposed no rate law. The rate law proposed by Katzer et al.^{1,9} predicts nitrogen formation rates 6-8 orders of magnitude smaller than the ones obtained by Gland et al.¹⁰ under the conditions of their experiments. Furthermore, this rate expression predicted a constant ratio of the formation rates of N_2 and N_2O equal to 2. Pignet and Schmidt^{6,11} studied the reduction of nitric oxide by ammonia at 0.115 torr between 400 and 1400 °C and reported that at high temperatures the NO consumption rate was proportional to $P_{\rm NO}P_{\rm NH_3}$ at high temperatures and found that NO inhibited the reaction as $P_{\rm NO}^{-1}$ at low temperatures.

From presently available results there is no single rate expression which fits rate data except over narrow ranges of parameters. The purpose of this paper is to examine the steady-state rates over a wide range of temperatures and feed compositions in order to determine whether a single rate expression will fit experimental rates and, if so, to infer the reaction mechanism responsible for these kinetics. We shall show that a single Langmuir-Hinshelwood expression fits all available data in the steady state. In the following paper we examine the spontaneous oscillations in rate which occur for certain ranges of parameters.

Experimental Section

Rates were measured in a 380-cm³ stainless-steel reaction cell whose partial pressures were monitored with a differentially pumped quadrupole mass spectrometer as described in detail elsewhere.^{12,13} The reactor residence time was 0.4 s or higher at a total operating pressure of 0.1-1torr with a background pressure less than 0.002 torr. Conversions were always less than 7% so that differential reactor behavior could be assumed. Reactor pressures were monitored with a McLeod gauge, and flow rates were measured by monitoring the pressure drop in chambers of known volume. The gases were purified as described elsewhere¹³ and premixed in these chambers.

Most kinetic data were obtained at a total pressure of 0.5 torr. For pressures below ~ 10 torr boundary layer effects and homogeneous reaction are negligible and mixing times were short compared to the reactor residence time. The catalyst was a resistively heated polycrystalline 0.025-cm diameter, high-purity Pt wire, 8-15 cm long (area $\approx 1 \text{ cm}^2$). The catalyst temperature was measured with a Pt-Pt-13% Rh thermocouple spot-welded to the center of the wire. An optical pyrometer was used to calibrate temperatures.

The only products observed below 850 °C were nitrogen. nitrous oxide, and water with a limit of detectability of 0.03%. Water was not monitored systematically. At temperatures higher than 850 °C, hydrogen formation

- Markvart, M.; Pour, V. L. J. Catal. 1967, 7, 279.
 Pignet, T.; Schmidt, L. D. J. Catal. 1975, 40, 212.
 Otto, K.; Shelef, M.; Kummer, J. T. J. Phys. Chem. 1970, 74, 2690.
 Otto, K.; Shelef, M.; Kummer, J. T. J. Phys. Chem. 1971, 75, 875.
- (9) Katzer, J. R. In "The Catalytic Chemistry of Nitrogen Oxides";
- Klimisch, R. L., Larson, J. G., Eds.; Plenum Press: New York, 1975; pp
- 133-66

(10) Gland, J. L.; Korchak, V. N. J. Catal. 1978, 55, 324.
 (11) Pignet T. Ph.D. Dissertation, University of Minnesota, Minneapolis, MN, 1974.

(12) Takoudis, C. G.; Schmidt, L. D., to be submitted.
 (13) Takoudis, C. G. Ph.D. Dissertation, University of Minnesota, Minneapolis, MN, 1981.

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⁽¹⁾ Putasen, R. J.; Katzer, J. R.; Manogue, W. H. Am. Inst. Chem. Eng. J. 1974, 20, 219.

⁽²⁾ Bauerle, G. L.; Nobe, K.; Koutsoukos, E. P. Atmos. Environ. 1974, 8, 1331

⁽³⁾ Bauerle, G. L.; Wu, S. C.; Nobe, K. Ind. Eng. Chem. Prod. Res. Dev. 1975, 14, 123.

⁽⁴⁾ Anderson, H. C.; Green, W. J.; Steele, D. R. Ind. Eng. Chem. 1961, 53, 199.



Figure 1. Nitrogen and nitrous oxide formation rates and nitric oxide consumption rate as functions of platinum temperature for a reaction mixture containing a large excess of nitric oxide. Solid curves are drawn to connect points and the dashed line is the one predicted from stoichiometry by adding the two formation rates and using the stoichiometries shown in eq. 1 and 2.

indicated NH_3 decomposition except in large excesses of nitric oxide. The mass spectrometer sensitivity for all gases was calibrated with gas mixtures of known compositions.

A minicomputer was used for controlling the wire temperature under conditions where spontaneous rate oscillations occurred. All reported reaction rates in that temperature range and feed gas compositions are time-averaged. A detailed discussion of oscillatory phenomena is reported in the following paper.

In a typical experiment the wire was first cleaned by heating to 1300 °C in O_2 at 0.015 torr for 10–15 min. Following this treatment Auger electron spectroscopy studies¹³ showed that the catalyst surface was free of any contamination (mainly carbon and calcium), and electron microscopy showed that surfaces were essentially smooth. Data were reproducible to within ±15% on eight different platinum wires.

Results

The nitrogen and nitrous oxide formation rates and the nitric oxide consumption rate vs. wire temperature are shown in Figure 1 for a large excess of NO in the gas phase $(P_{\rm NO}/P_{\rm NH_3} = 9)$, in Figure 2 for an excess of NH₃ in the feed mixture $(P_{\rm NO}/P_{\rm NH_3} = 1)$, and in Figure 3 for a feed mixture composition between the two stoichiometries of eq 1 and 2 $(P_{\rm N0}/P_{\rm NH_3} = 2.33)$. In all three cases the maximum N₂O formation rate occurs at a lower temperature than the one at which the maximum N_2 and NO rates occur. After these maxima, the rates decrease with increasing temperature for $P_{\rm NO}/P_{\rm NH_3}$ = 2.33 and 9, while for the case of excess of NH_3 in the feed mixture (Figure 2), as the temperature increases beyond 900 °C, the production (consumption) rate of N_2 (NO) levels off and then starts increasing again and H_2 formation is observed. When the amount of NH_3 in the feed mixture is increased, the N_2O formation rates decrease, whereas the production (consumption) rates of N₂ (NO) are highest at $P_{\rm NO}/P_{\rm NH_{*}}$ = 2.33. Also, a higher composition of NH_3 in the gas phase causes a shift of the maximum of the consumption (production) rate of NO (N_2) toward lower temperatures and decreases the initiation temperature for reaction between NO and NH₃.

In Figure 3 all three rates are shown to exhibit breaks in the temperature range of 400-470 °C which were reproducible at all times. These are associated with oscil-



Figure 2. N_2 and N_2O formation rates and NO consumption rate as functions of Pt temperature for a reaction mixture containing excess ammonia.



Figure 3. N_2 and N_2O formation rates and NO consumption rate as functions of Pt temperature for a reaction mixture between the two stoichiometries of eq 1 and 2.

lations which will be discussed in the following paper. Such breaks were also observed for $P_{\rm NO}/P_{\rm NH_3} = 1.5$ (stoichiometric mixture for eq 1) and 4 (stoichiometric mixture for eq 2). Notice that the solid lines in Figures 1-3 indicate lines connecting data for the formation rates of N₂ and N₂O, while the dashed line indicates the curve predicted from stoichiometry in each case by adding the two formation rates and using the stoichiometries shown in eq 1 and 2. The agreement between data obtained for the NO consumption and the stoichiometric curve is within $\pm 5\%$. Another observation from these figures is that the ratio of the two formation rates depends strongly on the temperature $T_{\rm S}$ and on the feed composition.

In Figure 4 the partial pressure of NH_3 is kept constant at 0.10 torr and the nitrogen formation rate is plotted vs. the NO partial pressure at three different temperatures, 400, 600, and 800 °C. At 800 °C this gives a straight line with a positive slope and indicates that the nitrogen production rate is first order in nitric oxide pressure at this temperature. At 600 °C, a curved line is observed and at



Figure 4. Nitrogen formation rate as a function of nitric oxide pressure. The rate is first order in nitric oxide pressure at 800 °C and nearly so at 600 °C.



Figure 5. Nitrogen formation rate as a function of ammonia pressure at 400, 600, and 800 $^\circ$ C. The rate is half order in ammonia pressure.

400 °C an almost horizontal line is obtained. These indicate that at lower temperatures NO inhibits the N₂ production strongly. Note that, for $P_{\rm NO} > 0.14$ torr, the N₂ formation rate goes through a maximum near 600 °C under constant partial pressures of NH₃ and NO. This also indicates strong NO inhibition of the N₂ production rate.

In Figure 5 the NO partial pressure is kept constant at 0.40 torr and the nitrogen production rate is plotted vs. the square root of the NH_3 partial pressure at wire temperatures of 400, 600, and 800 °C. At 400 °C the results give a straight line with a positive slope and indicate that the nitrogen formation rate is half order in ammonia pressure at this temperature. At 800 and 600 °C the results indicate almost straight lines with positive slopes. This shows that at these temperatures there is no NH_3 inhibition in the N_2 production. The nitrogen formation rate under constant NH_3 and NO partial pressures is shown to go through a maximum at 600 °C; this also indicates the strong NO inhibition in the nitrogen formation at low temperatures. Thus, Figures 4 and 5 show that at high temperatures

$$r_{\rm N_3} = k P_{\rm NO} P_{\rm NH_3}^{1/2} \tag{3}$$

where k depends on the temperature and partial pressures of NO and NH_3 .



Figure 6. Arrhenius temperature dependence of observed N_2 formation rate in excess nitric oxide at high temperatures.



Figure 7. Arrhenius temperature dependence of observed $N_{\rm 2}$ formation rate in excess nitric oxide at low temperatures.

In Figure 6, the quantity log $[r_{\rm N_2}/(P_{\rm NO}P_{\rm NH_3}^{-1/2})]$ is plotted vs. $10^3/T_{\rm S}$ at catalyst temperatures higher than 800 °C, at a total pressure of 0.5 torr for two different compositions, 10% and 20% NH₃, in the feed mixture. This yields a straight line and shows that NO inhibition is negligible at high temperatures in excess NO. The slope of this line yields an activation energy

$$E_1 = 7950 \pm 800 \text{ cal/mol}$$
 (4)

The intercept gives a preexponential factor

$$A_1 = 2.46 \times 10^{-7} \text{ mol}/(\text{cm}^2 \text{ s torr}^{3/2})$$
 (5)

Hence, we conclude that the nitrogen formation rate r_{N_2} at high temperatures and an excess of NO in the gas phase is described by

$$r_{N_2} (\text{mol}/(\text{cm}^2 \text{ s})) =$$

2.46 × 10⁻⁷ exp[(7950 ± 800)/RT]P_{NO}P_{NH_2}^{1/2} (6)

Note that, at high compositions of $\rm NH_3$ in the gas phase and high temperatures ($T_{\rm S} > 900$ °C), the ammonia decomposition reaction becomes important and the nitrogen formation rate increases more than that expected from eq 1.

It should be noted that rates are generally expected to decrease with increasing temperature as long as coverages are low and heats of adsorption are large compared to the reaction activation energy. For our model the LH mechanism predicts $r = k_{\rm R} K_{\rm NO} K_{\rm NH_3}^{1/2} P_{\rm NO} P_{\rm NH_3}^{1/2}$ at high temperatures. Therefore, the overall activation energy at high temperature should be $E_{\rm R} - \Delta H_{\rm NO} - 1/2 \Delta H_{\rm NH_3}$, which is negative for this system.

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In Figure 7, the quantity log $(r_{\rm Ng}P_{\rm NO}/P_{\rm NH_3})^{1/2}$ is plotted vs. $10^3/T_{\rm S}$ at low temperatures, $T_{\rm S} = 300-380$ °C, at a total pressure of 0.5 torr and for the same compositions as in Figure 6. The data yield a straight line and indicate that the nitrogen formation rate is minus first order in nitric oxide pressure at low temperatures with

$$E_2 = -23850 \pm 2000 \text{ cal/mol} \tag{7}$$

$$A_2 = 98.4 \text{ mol torr}^{1/2} / (\text{cm}^2 \text{ s})$$
 (8)

Thus, from Figures 6 and 7 we conclude that N_2 production should be described by the expression

$$r_{N_2} = A_1 \exp(E_1/RT) P_{NO} P_{NH_3}^{1/2} / [1 + A_{NO} \exp(E_{NO}/RT) P_{NO}]^2$$
(9)

where E_{NO} is the heat of adsorption of NO on the catalyst surface. Equations 4, 7, and 9 yield

$$E_{\rm NO} = (E_1 - E_2)/2 = 15900 \text{ cal/mol}$$
 (10)

while eq 5, 8, and 9 yield

$$A_{\rm NO} = 5 \times 10^{-5} \, \rm torr^{-1} \tag{11}$$

We noted from Figure 5 that no strong NH_3 inhibition was observed in N_2 formation. To study whether another term should be included in the denominator of eq 9, we used a nonlinear least-squares fitting technique¹¹ and found that data were best fitted by adding a term

$$\alpha \equiv K_3 P_{\rm NH_3}^{1/2} \tag{12}$$

where $K_3 = A_3 \exp(E_3/RT)$, and A_3 is in torr^{-1/2}. An Arrhenius plot of K_3 vs. $10^3/T_8$ yielded

$$E_3 = 5960 \text{ cal/mol} \tag{13}$$

$$A_3 = 0.0145 \text{ torr}^{-1/2} \tag{14}$$

Thus, from eq 9–14 we obtain the rate expression

a ...

$$r_{N_{2}} (mol/(cm^{2} s)) = (2.46 \times 10^{-7}) \times exp(7950/RT)P_{N0}P_{NH_{3}}^{1/2}/[1 + (5 \times 10^{-5}) \times exp(15900/RT)P_{N0} + 0.0145 exp(5960/RT)P_{NH_{3}}^{1/2}]^{2}$$
(15)

Equation 15 fitted all our data obtained at a total pressure of 0.5 torr, temperatures between 200 and 1200 °C, and feed compositions between $P_{\rm NO}/P_{\rm NH_3} = 1$ and 9, with ±15%. If a term of the form

$$\alpha' \equiv K'_{3} P_{\rm NH_3}^{1/4} P_{\rm NO}^{1/2} \tag{12a}$$

is used instead of the one shown in eq 12, as proposed by Gland and Korchak,¹⁰ the nitrogen formation rate expression fits all our data within $\pm 25\%$. Note that eq 15 predicts maximum reaction probability (rate of nitrogen formation/collision rate of limiting reactant) in the range 0.02–0.04 for temperatures between 500 and 600 °C.

Equation 15 was derived by analyzing data at 0.5 torr. In Figure 8, N₂ production rates are plotted vs. the catalyst temperature for three different pressures, 0.2, 0.5, and 1.0 torr. The solid lines represent predicted N₂ formation rates from eq 15. It is seen that the agreement between our data and predicted values is within $\pm 15\%$, for a feed composition $P_{\rm NO}/P_{\rm NH_3} = 4$ except at high temperatures. In Figure 9 we present our data and predicted values from eq 15 (solid lines) at a total pressure of 0.5 torr and 10%, 30%, and 50% NH₃ in the feed mixture, in a plot of N₂ formation rates vs. catalyst temperature. The agreement between our results and predictions is again within $\pm 15\%$.



Figure 8. Nitrogen formation rate as a function of platinum temperature at 0.2, 0.5, and 1.0 torr for a stoichiometric mixture of NH_3 and NO for eq 4.2. Solid lines are fits from the eq 15.



Figure 9. N_2 formation rate as a function of Pt temperature at 10%, 30%, and 50% NH₃ in the feed mixture. Solid lines are the fits from eq 15.

Another question remaining is which other reactions are significant under our conditions. These could be

$$2\mathbf{NH}_3 \to 3\mathbf{H}_2 + \mathbf{N}_2 \tag{16}$$

$$2NO \rightarrow N_2 + O_2 \tag{17}$$

$$N_2 O \rightarrow N_2 + \frac{1}{2}O_2 \tag{18}$$

$$4NH_3 + 6N_2O \rightarrow 8N_2 + 6H_2O$$
 (19)

In Figure 10 the rates of decomposition of $\rm NH_3, ^{14}$ NO, ¹⁵ and N₂O¹² are shown vs. the wire temperature on the same plot with the NO consumption rate during the reduction of NO by NH₃ at a total pressure of 0.5 torr and 20% NH₃ in the feed mixture. Rates for the unimolecular reactions of NO and NH₃ are for the same pressures as the partial pressures of these reactants in the bimolecular reaction. At temperatures less than 800 °C all three decomposition rates are at least 1 order of magnitude lower than the reaction between NO and NH₃. Separate studies of the reaction between N₂O and NH₃ at 0.5 torr and 17.5% and 38.5% NH₃ in the feed mixture were also carried out.¹³

⁽¹⁴⁾ Loffler, D.; Schmidt, L. D. J. Catal. 1976, 41, 440.

⁽¹⁵⁾ Mummey, M. J.; Schmidt, L. D. Surf. Sci. 1981, 109, 29.



Figure 10. NO consumption rate and NH_3 , NO, and N_2O decomposition rates as functions of Pt temperature using data from ref 14, 15, 12, and 13, respectively.

Below 750 °C and N_2O consumption rate was at least 1 order of magnitude slower than the reaction between NO and NH₃. This confirms that N_2 and N_2O are produced via two parallel reactions as shown in eq 1 and 2 and not via a series of two reactions. Figure 10 and data on the reaction between N_2O and NH₃ confirm that the stoichiometric curves shown in Figures 1–3 should be close to the data that we obtained for NO consumption rates.

Discussion

We have studied the reaction kinetics of the reduction of NO by NH₃ at pressures between 0.2 and 1.0 torr, temperatures between 200 and 1200 °C, and feed compositions between $P_{\rm NO}/P_{\rm NH_3}$ = 1 and 9 and have found that eq 15 predicts N₂ formation quantitatively. This equation indicates that the reaction is first order with respect to nitric oxide pressure and half order with respect to ammonia pressure if denominator terms are small. These results imply that dissociated ammonia and molecularly adsorbed nitric oxide are participating in the rate-limiting reaction for N_2 formation. The fact that dissociated ammonia participates in the rate-limiting step implies that adsorption and dissociation of the ammonia are occurring prior to the rate-limiting reaction. The rate equation 15 indicates that the nitric oxide inhibition pressure dependence is first order and the ammonia inhibition pressure dependence is probably of one-half order. In the range of temperatures and gas-phase concentrations studied, the third term in the denominator of eq 15 never became dominant so that ammonia inhibition was not important under any conditions of these experiments. Whenever a large excess of NH_3 was used, the reaction rate between NO and NH₃ was comparable to the NH₃ decomposition rate¹⁴ at pressures between 0.1 and 1.0 torr and temperatures between 400 and 1200 °C, so that reaction kinetic data could not be analyzed accurately. Otto et al.⁸ used ¹⁵N and suggested that the catalytic reduction of NO by NH₃ involves the following steps:

$$\mathbf{NH}_3 + \mathbf{2S} \rightleftharpoons \mathbf{NH}_2 - \mathbf{S} + \mathbf{H} - \mathbf{S}$$
(20)

$$NO + S \rightleftharpoons NO - S$$
(21)
$$NO - S + NH_{\circ} - S \rightarrow H_{\circ}O + N_{\circ} + 2S$$
(22)

$$NO-S + NH_{2}-S - \rightarrow N_{2}O + 2H-S \qquad (22a)$$

$$H-S + NO-S \rightarrow HNO-S + S$$
 (23)

$$2HNO-S \rightarrow N_2O + H_2O + 2S \qquad (24)$$

$$2HNO-S + 2H-S - - \rightarrow N_2 + 2H_2O + 4S \quad (24a)$$

where solid arrows in steps 22 and 24 represent major reaction paths, dashed arrows represent minor reaction paths, and S stands for an empty site on the catalyst surface. Katzer et al.¹ carried out experiments on supported Pt catalysts and reported results consistent with the reaction network proposed by Otto et al.⁸ Katzer et al. also proposed a rate expression for the N₂ formation which had the form

$$r_{\rm N_2} = K_{\rm R} P_{\rm NO} P_{\rm NH_3}^{1/2} / [1 + K_{\rm NO} P_{\rm NO} + K_{\rm NH_3}^{1/2} P_{\rm NH_3}^{1/2}]^2$$
(15a)

with negative activation energies for all K's. They also reported $r_{N_2}/r_{N_2O} = 2$ under all conditions. Although the general form of eq 15a is similar to eq 15, eq 15a predicted nitrogen formation rates 6-8 orders of magnitude smaller than the ones obtained by Gland et al.¹⁰ at much lower pressures. The reason for the negative heat of adsorption for NO used by Katzer et al. is also not clear. In all our experiments the ratio $r_{\rm N_2}/r_{\rm N_2O}$ depended on the temperature, the gas-phase composition, and the total reactor pressure so that a mechanism involving steps 20-24 does not explain our data. However, the N_2 formation rate expression shown in eq 15 fits our data to within $\pm 15\%$, it predicts the N₂ formation rates measured in ref 1, and it yields rates comparable to those reported in ref 10 at total reactor pressures between 10^{-9} and 10^{-8} torr. It also predicts a reasonable heat of adsorption for NO, $E_{\rm NO}$ = 15900 cal/mol.

Gland and Korchak,¹⁰ using a clean stepped platinum single crystal at pressures on the order of 10⁻⁸ torr, instead of eq 24 proposed the steps

$$HNO-S + H-S \rightarrow N-S + H_2O + S$$
(25)

$$2N-S \rightarrow N_2 + 2S \tag{26}$$

since no N_2O formation was observed under their conditions. They proposed the N_2 formation rate expression of the form

$$r_{\rm N_2} = K_1 P_{\rm NO} P_{\rm NH_3}^{1/2} / [1 + K_{\rm NO} P_{\rm NO} + K'_3 P_{\rm NH_3}^{1/4} P_{\rm NO}^{1/2}]^2$$
(27)

but they did not show fits of their rate expression to data. This mechanism does not fit our data over our ranges of variables because it cannot predict N₂O formation although a rate expression of the form shown in eq 27 fit our data within $\pm 25\%$.

We propose a more detailed mechanism

$$NH_{3} + 2S \xleftarrow{k_{*}}{k_{d}} NH_{2}-S + H-S$$
$$NO + S \xleftarrow{k'_{*}}{k'_{d}} NO-S$$
$$NH_{2}-S + NO-S \xrightarrow{k_{r}} N_{2} + H_{2}O + 2S$$
$$H-S + NO-S \xrightarrow{k_{4}} HNO-S + S$$
$$2HNO-S \xrightarrow{k_{5}} N_{2}O + H_{2}O + 2S$$

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HNO-S + H-S
$$\xrightarrow{R_6}$$
 N-S + H₂O + S
2N-S $\xrightarrow{k_7}$ N₂ + 2S

which is a combination of the two mechanisms discussed previously. No configurations should be inferred from postulated species. If $K_{\rm NH_3} \equiv k_{\rm a}/k_{\rm d}$, $K_{\rm NO} \equiv k'_{\rm a}/k'_{\rm d}$, adsorption-desorption equilibrium is assumed for NO and NH₃, and pseudosteady state is assumed for the adsorbed species HNO-S and N-S, then the formation rates of N₂ and N₂O are given by

$$\begin{aligned} r_{N_{2}} &= K_{NO}P_{NO}K_{NH_{3}}^{1/2}P_{NH_{3}}^{1/2} \times \\ &\left\{ k_{r} + \frac{k_{4}}{\epsilon} \left[\left(1 + \epsilon \frac{P_{NO}}{P_{NH_{3}}^{1/2}} \right)^{1/2} - 1 \right] \frac{P_{NH_{3}}^{1/2}}{P_{NO}} \right\} \right/ \\ &\left\{ 1 + K_{NO}P_{NO} + \left(\frac{k_{4}}{k_{7}} \frac{K_{NO}}{\epsilon} K_{NH_{3}}^{1/2} \right)^{1/2} \times \right. \\ &\left. P_{NH_{3}}^{1/2} \left[\left(1 + \epsilon \frac{P_{NO}}{P_{NH_{3}}^{1/2}} \right)^{1/2} - 1 \right]^{1/2} \right\}^{2} (28) \end{aligned}$$

 $r_{\rm N_2}/r_{\rm N_2O} = \{2/[(1 + \epsilon P_{\rm NO}/P_{\rm NH_3}^{1/2})^{1/2} - 1]\}\{(k_{\rm r}/k_4)[(1 + \epsilon P_{\rm NO}/P_{\rm NH_3}^{1/2})^{1/2} + 1] + 1\}$ (29)

where

$$\epsilon \equiv \frac{8k_4k_5}{k_6^2} \frac{K_{\rm NO}}{K_{\rm NH_3}^{1/2}}$$

Although eq 28 and 29 are complicated, they predict results reported in ref 1, 9, and 10 and in this paper.

Under ultrahigh vacuum where $P_{\rm NO}$ and $P_{\rm NH_3}$ are on the order of 10^{-8} torr, ${}^9P_{\rm NO}/P_{\rm NH_3}{}^{1/2}$ is on the order of 10^{-4} . Therefore, $\epsilon P_{\rm NO}/P_{\rm NH_3}{}^{1/2}$ is small and

$$\left(1 + \epsilon \frac{P_{\rm NO}}{P_{\rm NH_3}^{1/2}}\right)^{1/2} \approx 1 + \frac{\epsilon}{2} \frac{P_{\rm NO}}{P_{\rm NH_3}^{1/2}}$$
(30)

Hence

$$r_{N_{2}} = K_{NO}P_{NO}K_{NH_{3}}^{1/2}P_{NH_{3}}^{1/2}(k_{r} + k_{4}/2)/\{1 + K_{NO}P_{NO} + (k_{4}/2k_{7})^{1/2}K_{NO}^{1/2}P_{NO}^{1/2}K_{NH_{3}}^{1/4}P_{NH_{3}}^{1/4}\}^{2}$$
(28a)

$$\frac{r_{\rm N_2}}{r_{\rm N_2O}} = \frac{4}{\epsilon} \frac{P_{\rm NH_3}^{1/2}}{P_{\rm NO}} \left(2\frac{k_{\rm r}}{k_4} + 1\right)$$
(29a)

Equation 28a is eq 24 of ref 10 and, since $P_{\rm NO}/P_{\rm NH_3}^{1/2}$ is on the order of 10⁻⁴, one practically predicts only N₂ as a product, as has been observed at low pressures.

At atmospheric pressures and low temperatures $P_{\rm NO}/P_{\rm NH_s}^{1/2}$ is on the order of 1 but ϵ may become large so that

$$(1 + \epsilon P_{\rm NO} / P_{\rm NH_3}^{1/2})^{1/2} - 1 \approx (\epsilon P_{\rm NO} / P_{\rm NH_3}^{1/2})^{1/2}$$
 (31)

Then eq 28 and 29 become

$$r_{N_{2}} = k_{r} K_{NO} P_{NO} K_{NH_{3}}^{1/2} P_{NH_{3}}^{1/2} / \{1 + K_{NO} P_{NO} + (k_{4}/k_{7})^{1/2} (K_{NO}^{1/2} K_{NH_{3}}^{1/4} / \epsilon^{1/4}) P_{NO}^{1/4} (P_{NH_{3}}^{1/2})^{3/4} \}^{2}$$
(28b)

$$r_{\rm N_2}/r_{\rm N_2O} = 2k_{\rm r}/k_4$$
 (29b)

where r_{N_2}/r_{N_2O} is predicted to be independent of partial pressures. This has been reported in ref 1. Equations 28b

and 29b are similar to eq 1 and 2 of ref 1 and 9.

Under the conditions of our experiments, pressures on the order of 0.5 torr and temperatures between 200 and 1200 °C, we observed two products and that $r_{\rm N_2}/r_{\rm N_20}$ increases with increasing $P_{\rm NH_3}$ at constant total pressure and catalyst temperature (Figures 1-3). If $P_{\rm NO} = P_{\rm t} - P_{\rm NH_3}$ and $P_{\rm t}$ is the total reactor pressure, eq 29 implies

$$d(r_{N_2}/r_{N_2O})/dP_{NH_3} > 0$$
 (32)

Equations 29 and 32 combined with the observation of both N_2 and N_2O as products indicate that the term $\epsilon P_{NO}/P_{NH_3}^{1/2}$ is of the order of 1 at temperatures between 500 and 700 °C. At lower temperatures this term is large and eq 28 reduces to eq 28b, which is similar to eq 15. At higher than 700 °C temperatures this term is small and eq 28 and 29 reduce to eq 28a, which is similar to eq 15, and to eq 29a, respectively, so that N_2 would be mainly formed (Figures 1-3). At higher temperatures this term should become small so that only N_2 would be formed (eq 28a and 29a).

Equation 15 is obtained by assuming that the predominant surface species are nitric oxide and nitrogen, as observed¹⁰ by thermal desorption studies at 10^{-8} torr. Thus, the second term in the denominator of eq 15 corresponds to the surface coverage of NO and the third term corresponds to the nitrogen surface coverage. Hence, K_3 does not necessarily have to be equal to $K_{\rm NH_3}^{1/2}$ because it involves more than one rate constant.

Summary

The reaction between nitric oxide and ammonia at pressures on the order of 0.5 torr proceeds rapidly in the 400–800 °C range, and the only products observed are molecular nitrogen and nitrous oxide. The rate-limiting reaction for the N_2 formation is postulated to occur between an adsorbed fragment of NH_3 and adsorbed molecular nitric oxide, although detailed spectroscopic characterization would be needed to confirm this interpretation.

All steady-state rate measurements in the NO + NH_3 reaction on Pt between 10⁻⁸ and 10³ torr^{1,10} obtained in our and other experiments can be explained by a single and reasonable Langmuir-Hinshelwood reaction scheme. The elementary reaction steps and intermediates also seem to be reasonable. The only unpredictable feature of our experimental data is the existence of breaks in the consumption (formation) rates of NO $(N_2 \text{ and } N_2O)$ vs. the catalyst temperature at high coverages where rate oscillations occur, as will be described in the following paper. Such breaks also indicate that the adsorption-desorption equilibrium assumption in some steps of the model is invalid in some situations. 13,16 At very low pressure no N_2O formation was observed; in our studies (0.2-1.0 torr) the ratio $r_{\rm N_2}/r_{\rm N_2O}$ was typically between 3.5 and 20.0 in the temperature range 280-600 °C, and at atmospheric pressures r_{N_2}/r_{N_2O} was equal to 2 as predicted by eq 29, 29a, and 29b.

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⁽¹⁶⁾ Takoudis, C. G.; Schmidt, L. D.; Aris, R. Chem. Eng. Sci. 1981, 36, 377.