**The Kinetics of the NH Reaction with H₂ and Reassessment of HNO Formation from
NH + CO₂, H₂O.**

Arthur Fontijn,* Sayed M. Shamsuddin,[†] Duane Crammond[§]

*High-Temperature Reaction-Kinetics Laboratory, The Isermann Department of Chemical
and Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180-
3590*

Paul Marshall*

*Department of Chemistry, University of North Texas, P.O. Box 305070, Denton, TX
76203-5070*

William R. Anderson*

*AMSRD-ARL-WM-BD, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD
21005-5069*

*corresponding authors email addresses: fontia@rpi.edu, marshall@unt.edu,
willie@arl.army.mil

[†]On leave from Department of Applied Chemistry and Chemical Technology.
University of Dhaka, Dhaka-1000, Bangladesh

[§]Deceased

Abstract

The reaction of ground state NH with H₂ has been studied in a high-temperature photochemistry (HTP) reactor. The NH (X³Σ) radicals were generated by the 2-photon 193 nm photolysis of NH₃, following the decay of the originally produced NH(A³Π) radicals. Laser-induced fluorescence on the NH(A³Π-X³Σ 0,0) transition at 336 nm was used to monitor the progress of the reaction. We obtained k (833-1432 K) = $3.5 \times 10^{-11} \exp(-7758 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with $\pm 2\sigma$ precision limits varying from 12 to 33% and corresponding accuracy levels of 23 to 39%. This result is in excellent agreement with that of Rohrig and Wagner [Proc. Comb. Inst. 25 (1994) 993 [1] and the data sets can be combined to yield k (833 - 1685 K) = $4.4 \times 10^{-11} \exp(-8142 \text{ K}/T)$. Starting with this agreement, it is argued that their [1] rate coefficients for NH + CO₂ could not be significantly in error. This, combined with models of several combustion systems, indicates that HNO + CO cannot be the products, contrary to their suggestion[1]. *Ab initio* calculations have been performed which confirm this conclusion by showing the barriers leading to these products to be too high compared to the measured activation energies. The calculations indicate the likelihood of formation of adducts, of low stability. These then may undergo further reactions. The NH + H₂O reaction is briefly discussed and it is similarly argued that HNO + H₂ cannot be the products, as had been previously suggested.

1. Introduction

Knowledge of the kinetics of reactions of, or leading to, NH is important in combustion research. For the title reactions the apparently only direct observations are those of Rohrig and Wagner, who studied these reactions within the 1100-2000 K temperature range behind shock waves[1]. NH in its ground electronic state ($X^3\Sigma$) was produced by thermal dissociation of HN_3 . Its concentration was monitored by cw laser absorption. For the reaction

they obtained $k_1(1156\text{-}1685 \text{ K}) = (1.7 \pm 0.8) \times 10^{-10} \exp(-10,100 \pm 200) \text{ K}/T$, for

they determined $k_2(1201\text{-}1912 \text{ K}) = (1.7 \pm 0.8) \times 10^{-11} \exp(-7220 \pm 200) \text{ K}/T$, and for

they measured $k_3(1329\text{-}1906 \text{ K}) = (3.3 \pm 1.6) \times 10^{-11} \exp(-6970 \pm 200) \text{ K}/T$. Here the rate coefficients are expressed in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The heats of formation are taken from the JANAF tables[2], except for NH, NH_2 , and HNO, which are from Anderson[3,4].

For reaction (2), Rohrig and Wagner concluded that $\text{HNO} + \text{CO}$ are the products of the CO_2 reaction, as all other product channels they considered are too endothermic in view of the observed activation energy. For reaction (3), they identified several other energetically accessible channels, but considered the products shown as the most likely. There are, however, several difficulties with these conclusions. When either or both of the reverse reactions (-2) or (-3) with $k_{-2}(T)$ and $k_{-3}(T)$ determined from the above expression and the thermochemistry are used in models of several combustion systems, global reaction rates are too fast by one to four orders of magnitude; detailed analysis revealed in all cases that the problem is intimately connected to the inclusion of these reverse processes. These models include: (i) that of

Glarborg *et al.* [5] for NO reduction in rich NO/CO/H₂ mixtures, in two flow reactors, for the 1200 to 1800 K temperature domain, (ii) that of Dagaut *et al.* [6] for such mixtures in a jet stirred reactor from 800 to 1400 K, and (iii) Anderson's calculations of the Diau *et al.* [7] results on the thermal reduction of NO by H₂ in mixtures of these compounds with CO in a static reactor from 900 to 1225 K (See Appendix). Models for the thickness of dark zones in nitrate ester propellants combustion are similarly very adversely affected[8]. All these groups achieved good comparisons of models with experiments without reactions (-2) and (-3), suggesting that the products and/or rate coefficients are incorrect, and thus decided to omit them and their assumed reverse processes.

It thus appears that either the reported rate coefficients are incorrect or that the products of the NH reactions with CO₂ and H₂O are not those indicated by equations (2) and (3). In order to decide between these possibilities we have now studied one of their [1] reactions, i.e. that with H₂, by a very different experimental technique, and have made an *ab initio* study of reaction (2). The results indicate that HNO + CO and HNO + H₂ are not the products of reactions (2) and (3), respectively. Much further work will be necessary to identify the actual product channels.

2. The NH + H₂ reaction

2.1 Experimental technique

A schematic of the HTP reactor used is shown in Figure 1. It and the data acquisition procedures have been described frequently[9,10]. Briefly, the 5 cm i.d., 30 cm long ceramic reaction tube is surrounded by resistance heating elements and insulation in a stainless steel vacuum chamber. The bottom (upstream) plate contains an inlet for N₂ bath gas and a water-cooled inlet through which the photolyte NH₃ and the second reactant gas, here H₂, flow separately. Teledyne-Hastings mass flow controllers are used, and pressure is measured with an MKS Baratron transducer. The linear gas velocities, $\bar{v}$, are fast enough to provide each

photolysis pulse with a fresh reaction mixture. Residence times between the cooled inlet and the observed reaction zone are long compared to the reaction times and are chosen such that mixing is at least 99% complete[11, 12].

The reactor contains four side ports at right angles. Two facing ports have Brewster angle windows through one of which the 193 nm photolysis laser radiation (Lambda Physik Compex 201) is introduced. The other window provides the entrance port for the collinear diagnostic beam from a Lambda Physik LPX 100 excimer FL 3002 dye laser combination. The photolysis radiation can be focused on the center of the reaction tube with a plano-convex lens. The dye laser is tuned to 336 nm to pump the $\text{NH}(\text{A}^3\Pi-\text{X}^3\Sigma\ 0,0)$ transition. The resulting fluorescence is observed with an EMI 9813 QA photomultiplier tube. The PMT signal is processed with Stanford Research SR 250 boxcar integrators, which provide a range of delay times from the photolysis pulse.

The experiments were carried out under pseudo-first-order conditions, with $[\text{NH}] \ll [\text{H}_2] \ll [\text{N}_2]$. Under these conditions, the fluorescence intensity I , which is proportional to $[\text{NH}]$, is expressed by

$$I = I_0 \exp(k_{psl}t) + B \quad (4)$$

Here k_{psl} is the pseudo-first-order rate coefficient, $I_0 + B$ is the intensity at time $t = 0$, and B is the background, due mainly to scattered light. The values of k_{psl} were obtained by a weighted fit of the observed I vs t profiles to eq (4). [13] Typically, five k_{psl} measurements at varying $[\text{H}_2]$ were used to obtain the bimolecular rate coefficients, k_i , at the temperature and pressure of the experiment. The minimum $[\text{H}_2]$ were set ca. 5 times lower than the maximum values listed in Table 1. The exponentiality of the I vs. t plots was tested by a two-stage residual analysis[14]. The analysis consists of a visual inspection of the residual plot followed by the runs test. A new objective validation method, based on the combination of the chi-square goodness-of-fit and

bootstrap (similar to the Monte Carlo) method, is also used[15]. The two methods have been found to be nearly always in agreement.

The gases used were N₂ (99.995% from the liquid), and NH₃ (99.995%) from Praxair and H₂ (99.999%) from Matheson. The H₂ was dried by passing through drierite. The NH₃ was used as 0.3% NH₃ in N₂, premixed in the laboratory.

2.2 NH production

There are a variety of means of producing NH in the literature, most of which are not suitable for photolysis experiments at or near combustion temperatures. The method developed here is based on the observation, by Kenner *et al.* [16], that 193 nm two-photon photolysis of NH₃ proceeds in part as $\text{NH}_3 + h\nu \rightarrow \text{NH}_2^* + \text{H}$ followed by $\text{NH}_2^* + h\nu \rightarrow \text{NH}(\text{A}^3\Pi) + \text{H}$. The NH(A³Π) has a radiative lifetime of $4.2 \times 10^{-7}\text{s}$ [17]. Hence, on a time scale short compared to the $\gtrsim 10^{-4}\text{s}$ of the present experiments, the photolysis leads to NH(X³Σ). There is also some direct formation of NH(X³Σ), as well as of the singlet states NH(a¹Δ) and of NH(b¹Σ)[18]. The a state has been shown to be quenched by N₂ [19], $k_Q(300\text{ K}) = (6-9) \times 10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1}$, which was therefore used as the bath gas and as the NH₃ diluent. The highest NH fluorescence intensities were obtained by slightly defocusing the photolysis laser beam. Apparently this reduced photolysis of NH.

2.3 Results and Discussion

The measured rate coefficients, and the conditions under which they were obtained, are given in Table 1. To verify that the rate coefficients are independent of the reaction parameters, plots of residuals $[k(T) - k_i]/k(T)$ versus these parameters were prepared. Here, $k(T)$ represents the rate coefficients obtained from the fit expression eq. (5) below, and k_i are the individual rate coefficients measured. The parameters thus checked are: P, total pressure; [M], the corresponding total gas concentration; the second reactant and photolyte concentration; LP, the

photolysis laser power; z , the cooled inlet to observation plane distance; $\bar{v}$, the average gas velocity; the corresponding residence time t ; the products $\text{LP}[\text{H}_2]$ and $\text{LP}[\text{NH}_3]$, and T^{-1} . These residual plots are found to be independent of these parameters.

Figure 2 shows the present data. These may be fitted by the Marquardt algorithm [20] to the form $A \exp(-E_A/T)$, where σ_{k_i} and $\sigma_T/T = \pm 2\%$ contribute to the weighting of each point. The fitted expression is

$$k_1(833 - 1432 \text{ K}) = 3.49 \times 10^{-11} \exp(-7758 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

The variances and covariances are $\sigma_A^2 = 1.8332 \times 10^{-1} \text{ A}^2$, $\sigma_E^2 = 2.3096 \times 10^5$, and $\sigma_{AE}^2 = 203.6 \text{ A}$. The resulting 2σ precision levels of the fit are between ± 12 and $\pm 33\%$. Allowing liberally for $\pm 20\%$ systematic errors yields accuracy levels from ± 23 to $\pm 39\%$.

Also shown in Fig. 2 are the 1156 – 1685 K data from Rohrig and Wagner for this reaction. The agreement is very good so that the two data sets can be combined, which yields

$$k_1(833 - 1685 \text{ K}) = 4.34 \times 10^{-11} \exp(-8142 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

Those authors also noted fair agreement with k_1 and k_{-1} data obtained by fitting observations in more complex environments, i.e. for reaction (1) in the 2600-2800 K range [21] and from the reverse reaction [35, 36] also at higher temperatures.

3. The $\text{NH} + \text{CO}_2$ Reaction

3.1 The rate coefficients

The fact that two very different techniques (HTP and shock tube) using different NH production method (NH_3 photolysis and HN_3 thermal dissociation) yield such excellent agreement for $k_1(T)$ makes it unlikely that there can be a basic error in the technique used for the Rohrig and Wagner measurements on reaction (2). It should be considered if other processes could have significantly influenced their NH - consumption measurements. Conceivably, O

atoms from CO₂ dissociation could have interfered due to the very fast reaction of O with NH, leading to NO + H and OH + N, for which the rate coefficients are near the gas kinetic collision rate coefficients, i.e. on the order of $1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, essentially independent of temperature in the range of interest [22]. However, extrapolated CO₂ dissociation data [23] down to 1912 K, indicate the [O] to be too small by several orders of magnitude to have influenced their [1] results. For an impurity to have caused the measured rates, these would have to have been introduced with the CO₂, as the comparison above for the H₂ reaction suggests no such effect on those experiments. The purity of their CO₂ was [1] 99.995%. Hence any impurity from that source could only have led to rate coefficients orders of magnitude smaller than those observed.

Thus, since the $k_2(T)$ data appear substantiated, the assignment of the reaction products as HNO + CO has to be the cause of the discrepancy between the results of Ref. 1 and the combustion modeling studies mentioned in the Introduction. To investigate this further, *ab initio* studies have been performed (see below). It may also be mentioned that we attempted to measure $k_2(T)$ by the same technique as used for $k_1(T)$. However, in this case O atoms were found to be produced in the photolysis process, which could interfere and this approach was not pursued further.

3.2 *Ab initio calculations and discussion*

Reactants, products, transition states and potential intermediates were characterized with the GAUSSIAN98 program suite[24]. First, geometries and vibrational frequencies were derived at the B3LYP level of hybrid density functional theory, using the 6-311G(d,p) atomic basis set. Second, single point energies were obtained by approximate extrapolation of coupled-cluster theory to the complete basis set limit, via application of the CBS-QB3 approach of

Petersson and co-workers[25]. These energies, together with zero-point vibrational and thermal corrections, yield enthalpies relative to the reactants, $^3\text{NH} + \text{CO}_2$, at 298 K.

Some of the *ab initio* results are summarized in Figs. 3 and 4; complete structural details are given in the Supplementary Material. Table 2 lists the CBS-QB3 enthalpies at 298 K and the enthalpies relative to reactants for all adduct species found; these adducts are shown in Fig. 4. The first 7 structures are singlet molecules; CIS/6-311G(d,p) calculations indicate that in each case the lowest triplet energy is higher. Structure 8 of Fig. 4 is a triplet adduct between NH and CO_2 .

Figure 3 shows potential energy diagrams for the reaction of triplet and singlet NH with CO_2 . Spin-allowed abstraction to form triplet HNO is possible, but there is a large barrier of 226 kJ mol^{-1} . If intersystem crossing to a singlet surface occurs early in the reaction, then a cyclic adduct, with N attached across a C-O bond, can form, shown as 1 in Figs. 3 and 4. This adduct is too weakly bound, by only 8 kJ mol^{-1} relative to reactants, to be a final sink for ^3NH , but it can undergo further chemistry. The NH group can insert into the C-O bond over a barrier of 126 kJ mol^{-1} to form another adduct, shown as 7 on Figs. 3 and 4. In turn, this second adduct can rearrange while traversing a small barrier and dissociate to $^1\text{HNO} + \text{CO}$. Both these paths to $\text{HNO} + \text{CO}$ exhibit major barriers in excess of the endothermicity, and therefore are inconsistent with the measured activation energy, 60 kJ mol^{-1} , corresponding to Eq. 2.

The calculations thus confirm the conclusion from the combined experimental and modeling work that $\text{HNO} + \text{CO}$ can not be the products of the $\text{NH} + \text{CO}_2$ reaction.

An alternative product path is creation of a stable or intermediate adduct. We have tried a variety of initial geometries and from these derived optimized geometries of 8 candidates, which are drawn in Fig. 4. Their enthalpies relative to $^3\text{NH} + \text{CO}_2$ are summarized in Table 2. The

most stable is the HONCO structure 4, but even this is only exothermic by 33 kJ mol⁻¹. It is therefore insufficiently stable to act as a permanent sink for NH at elevated temperatures.

The known thermochemistry in this system provides a check on the accuracy of the *ab initio* calculations. The overall enthalpy change at 298 K for HNO + CO formation is computed to be +30 kJ mol⁻¹, in accord with the thermochemical value of +33 kJ mol⁻¹. As a second check, the enthalpy change for ³NH + CO₂ → HCN + O₂ is computed to be +166 kJ mol⁻¹, again in good agreement with the literature based value [2, 3] of + 172 kJ mol⁻¹. Computed ΔH_{298}^0 values therefore seem to be usefully reliable. An empirical estimate of the singlet-triplet gap in NH is 150 kJ mol⁻¹ and prior theoretical work suggests higher values of 157 and 170 kJ mol⁻¹ [26]. Degenerate orbitals make ¹NH inappropriate for the single-reference treatments applied here; nevertheless the computed adiabatic singlet-triplet gap of 170 kJ mol⁻¹ is close to these prior estimates. In the case of HNO, the singlet-triplet gap is predicted to be 77 kJ mol⁻¹, which is equal to the value derived from a chemiluminescence spectrum[27]. Somewhat lower theoretical values led Gurvich *et al.* to recommend 72 ± 6 kJ mol⁻¹[28]. The magnitude of this gap makes the spin-allowed path for the NH + CO₂ reaction going to triplet HNO + CO over 100 kJ mol⁻¹ endothermic, which is incompatible with the observed activation energies.

4. The NH + H₂O Reaction

While we have not explicitly studied this reaction a few remarks about it can be made. Regarding the rate coefficients, one possible concern is that H₂O might have dissociated thermally in the shock experiments. However, calculations based on recommended rate coefficients [29, 30] indicate the H₂O dissociation products, H and OH, would have been present in far too small concentrations to have substantially reduced [NH]. Highly purified H₂O was used [1] and a major impurity effect on the rate coefficients is again highly unlikely. Thus, the discrepancy with the models can reasonably be attributed to the products not being HNO + H₂.

In this case, alternate energetically accessible addition products, H_3NO and H_2NOH have been suggested [1], but these possibilities need further study.

5. Conclusions

Using an independent technique, the $\text{NH} + \text{H}_2$ rate coefficients of Rohrig and Wagner have been confirmed and the temperature range of the observations has been extended. This leads to the conclusion that their $\text{NH} + \text{CO}_2$ and $\text{NH} + \text{H}_2\text{O}$ rate coefficients are also beyond reasonable doubt. However, as discussed in the Introduction and further in the Appendix, modeling of three experiments (Refs. 5,6 and the present modeling of Ref. 7) and of propellant dark zones is adversely affected if either or both of reactions (2) and (3) and their reverse processes are included in the mechanisms. Detailed analysis indicates in all cases that this is due to the reverse reactions providing a radical source which causes a vast over-prediction of the global chemical rates. Excellent results are achieved when these reactions are omitted. These observations thus indicate that the products cannot be $\text{HNO} + \text{CO}$ or $\text{HNO} + \text{H}_2$, respectively.

Furthermore, *ab initio* calculations of the potential energy surfaces for the $\text{NH} + \text{CO}_2$ reaction were performed in the present work. These show that the barriers leading to $\text{HNO} + \text{CO}$ products are much too high to agree with the activation energy measured in Ref. 1. The calculations also indicate that adducts can form. These may undergo further reaction. However, since no unique products have been identified, other types of experiments and/or more extensive *ab initio* calculations are desirable.

Acknowledgement

The work at Rensselaer was supported by the ARO under grants DAAD 19-03-1-0046 and DAAD 19-99-1-0209. PM thanks the NSF (Grant CTS-0113606) and Welch Foundation (Grant B-1174) for support. Computational facilities were provided on the UNT Academic Computing Services' Research Cluster, and by the National Center for Supercomputing Applications (Grant

CHE000015N). We thank Dr. P. Glarborg for helpful discussions and him and Dr. P. Dagaut for showing us Ref. 6 before publication and W.F. Flaherty, A. Cosic, and R. Frimpong for assistance with the work. We also wish to acknowledge Drs. A. Fernandez, B. Cosic, and A. Hanf for their active interest during the course of this research.

References

- [1] M. Rohrig, H.G. Wagner, *Proc. Comb. Inst.* 25 (1994) 975.
- [2] M.W. Chase, Jr., Ed; NIST-JANAF Thermochemical Tables, 4th ed.; J. Phys. Chem. Ref. Data, Monograph 9; American Chemical Society; Washington, D.C., 1998.
- [3] W.R. Anderson, *J. Phys. Chem.* 93 (1989) 530.
- [4] W.R. Anderson, *Combust. Flame* 117 (1999) 394.
- [5] P. Glarborg, P.G. Kristensen, K. Dam-Johanson, M.U. Alzueta, A. Millera, R. Bilbao, *Energy & Fuels* 14 (2000) 828.
- [6] P. Dagaut, F. Lecomte, J. Mieritz, P. Glarborg, *Int. J. Chem. Kinet.* 35 (2003) 564.
- [7] E.W. Diau, M.J. Halbgewachs, A.R. Smith, M.C. Lin, *Int. J. Chem. Kinet.* 27 (1995) 867.
- [8] W.R. Anderson, A. Fontijn, in: *Overviews of Recent Research on Energetic Materials*; R.W. Shaw, T.B. Brill, D.L. Thompson, Eds., World Scientific, London, Chap. 7, (2005).
- [9] K. Mahmud, J.-S. Kim, A. Fontijn, *J. Phys. Chem.* 94 (1990) 2994.
- [10] A.S. Narayan, A.G. Slavejko, A. Fontijn, *Proc. Comb. Inst.* 24 (1992) 727.
- [11] P.S. Riley, B. Cosic, A. Fontijn, *Int. J. Chem. Kinet.* 35 (2003) 374.
- [12] P. Marshall, T. Ko, A. Fontijn, *J. Phys. Chem.* 93, (1989) 1922.
- [13] P. Marshall, *Comput. Chem.* 11 (1987) 219.
- [14] T. Ko, G.Y. Adusei, A. Fontijn, *J. Phys. Chem.* 95 (1991) 8745.
- [15] Fernandez, A., Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, N.Y., 2002.
- [16] R.D. Kenner, F. Rohrer, R.K. Browarzik, A. Kaes, F. Stuhl, *Chem. Phys.* 118 (1987) 141.
- [17] E.C. Chappell, J.B. Jeffries, D. Crosley, *J. Chem. Phys.* 97 (1992) 2400.

- [18] R.D. Kenner, F. Rohrer, F. Stuhl, J. Chem. Phys. 86 (1987) 2036.
- [19] K. Yamasaki, S. Okada, M. Koshi, H. Matsui, J. Chem. Phys. 95 (1991) 5087.
- [20] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, Numerical Recipes; Cambridge University Press: New York, (1986), Chap. 14.
- [21] J.E. Dove, W.S. Nip, Can. J. Chem. 57 (1979) 689.
- [22] D. L. Baulch, C. T. Cobos, R. A. Cox, P. Frank, G. Hayman, Th. Just, J. A. Kerr, T. Murrells, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, J. Phys. Chem. Ref. Data 23 (1994) 847.
- [23] M. Burmeister, P. Roth, AIAA J. 28 (1990) 402.
- [24] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, M.; R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, D. Martin, J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.9; Gaussian, Inc., Pittsburgh, PA, 1998.
- [25] J.A. Montgomery, Jr., M.J. Frisch, J.W. Ochterski, G.A. Petersson, J. Chem. Phys. 110 (1999) 2822.
- [26] K.P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules; van Nostrand Reinhold, New York, 1979.
- [27] T. Ishiwata, H. Akimoto, I. Tanaka, Chem. Phys. Lett. 27 (1974) 260.
- [28] L.V. Gurvich, I.V. Veyts, C.B. Alcock, Thermodynamic Properties of Individual Substances, 4th Edition; Hemisphere, New York, Vol. 1, 1989.
- [29] D.L. Baulch, C.J. Cobos, R.A. Cox, P. Frank, Th. Just, J.A. Kerr, M.J. Pilling, J. Troe, R. W. Wacker, J. Warnatz, J. Phys. Chem. Ref. Data 21 (1982) 411.
- [30] N. Cohen, K.R. Westberg, J. Phys. Chem. Ref. Data 20 (1991) 1211.
- [31] J.A. Miller, C.T. Bowman, Progr. Energy Combust. Sci. 15 (1989) 287.
- [32] A. Fontijn, A. Goumri, A.Fernandez, W.R. Anderson, N.E. Meagher, J. Phys. Chem. 104 (2000) 6003.

- [33] N.E. Meagher, W.R. Anderson, J. Phys. Chem. 104 (2000) 6013.
- [34] A.E. Lutz, R.J. Kee, J.A. Miller, Sandia National Laboratories Technical Report SAND87-8248, October 1988.
- [35] D.F. Davidson, K. Kohse-Hoinghaus, A.Y. Chang, R.K. Hansen, Int. J. Chem. Kinet. 22 (1990) 513.
- [36] M. Yumura, T. Asaba, Proc. Comb. Inst. 18 (1981) 863.

Appendix. Significance of Reactions (-2 and -3).

As mentioned in the Introduction, inclusion of k_{-2} and/or k_{-3} can cause models to strongly deviate from experiments. This may be illustrated by the effect of using k_{-2} or k_{-3} in the model for CO_2 production in $\text{NO}/\text{H}_2/\text{CO}$ mixtures, diluted in Ar, as measured by Diau *et al.*[7]. The base mechanism used was developed for propellant combustion[8]. It is based on that of Miller and Bowman [31] for nitrogen chemistry in combustion, as further extended in Refs. 32 and 33. The modeling utilizes the SENKIN time-dependent, homogeneous gas-phase reaction code[34]. The thermochemistry is taken from Refs. 2-4. Figure 5a shows that there is good agreement between the calculated $[\text{CO}_2]$ using this base model and the experimental results. Conditions are 0.960 bar, 1000 K and initial mole fractions of H_2 , NO , and CO of 0.0263, 0.0161, and 0.0430, respectively.

Figure 5b shows the effect of adding $\text{HNO} + \text{CO} \rightarrow \text{NH} + \text{CO}_2$ to the model, assuming its rate to be determined via the k_2 of Ref. 1 and the thermochemistry. The CO_2 production rate increases by a factor 10^4 . Figure 5c shows the effect of instead adding $\text{HNO} + \text{H}_2 \rightarrow \text{NH} + \text{H}_2\text{O}$ to the model, again assuming the rate to be determined via the k_3 of Ref. 1 and the thermochemistry. The CO_2 production rate increases by a factor 10^3 . The error becomes cumulatively worse if the two reactions are added together (not shown). Similar erroneous results are obtained for other experimental conditions of Diau *et al.* Therefore, the actual rates of these two HNO reactions appear to be vanishingly small.

The possibility that an error in the thermodynamics used in reversing Reactions (2) or (3) might have contributed to the over-prediction of the global rate was checked by assuming an error of 20 kJ mol⁻¹ in their heats of reaction. This is at least a factor of 5 larger than the error limits in the heats of formation would permit. For the conditions of Fig. 5, the error in either of the computed reverse rate coefficients would be about a factor of 10. Using this factor in the calculation [inputting Reactions (2) and (-2) or (3) and (-3) as separate, one-way reactions to CHEMKIN and reducing the rate coefficient for (-2) or (-3)], the time for CO₂ growth is increased (and, thus, the reaction rate decreased) in both cases by about a factor of 10. The rate is still far over-predicted.

Supporting Information available: Table 1S lists Cartesian coordinates for the adducts and transition states shown in Figs. 3 and 4, derived at the B3LYP/6-311G(d,p) level of theory.

Table 1: Summary of the rate coefficient measurements of the $\text{NH}(\text{X}^3\Sigma) + \text{H}_2 \rightarrow \text{NH}_2 + \text{H}$ reaction

T, K	P, mbar	[M], 10^{18} cm^{-3}	$[\text{H}_2]_{\text{max}}$, 10^{16} cm^{-3}	LP, mJ	$[\text{NH}_3]$, 10^{14} cm^{-3}	z, cm	$\bar{v}$, cm s^{-1}	$(k_i \pm \sigma_{k_i})$, $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
833	138	1.20	9.71	75	5.37	12	23.1	0.47 ± 0.11
869	219	1.82	6.35	81	9.43	16	14.9	0.30 ± 0.23
934	305	2.36	15.4	111	6.90	12	11.5	0.69 ± 0.14
978	181	1.34	12.2	24	5.05	12	21.2	1.07 ± 0.17
1025	138	0.97	8.08	66	4.25	12	28.4	2.16 ± 0.35
1045	162	1.13	7.40	93	5.00	8	24.2	2.68 ± 0.21
1113	313	2.04	13.1	101	5.96	12	13.3	3.38 ± 0.53
1155	163	1.02	7.47	102	3.00	8	26.4	3.55 ± 0.92
1174	144	0.89	2.65	90	2.73	16	30.2	2.96 ± 0.33
1265	173	0.82	5.28	60	3.30	12	33.3	10.6 ± 1.2
1368	278	1.47	6.93	108	6.67	8	18.1	11.9 ± 1.3
1432	72	0.36	2.11	123	1.57	12	74.2	16.6 ± 2.8

Table 2: *Ab initio* enthalpies for stable HNC₂ species derived via the CBS-QB3 method.

molecule	CBS-QB3 enthalpy at 298 K, au ^a	Enthalpy relative to ³ NH + CO ₂ at 298 K, kJ mol ⁻¹
1	-243.51270	-8
2	-243.48645	+61
3	-243.49393	+41
4	-243.52232	-33
5	-243.47184	+99
6	-243.36024	+392
7	-243.46509	+117
8	-243.42968	+210

^a 1 au $\approx$ 2625.5 kJ mol⁻¹

FIGURE CAPTIONS

Figure 1. Schematic of the HTP reactor.

Figure 2. Arrhenius plot of the $\text{NH} + \text{H}_2$ rate coefficients

○ k , present work
 ▲ k , Rohrig and Wagner [1]
 — best fit to all data, Eq. (6)

Figure 3. Potential energy diagram for $\text{NH} + \text{CO}_2$ showing paths to $\text{HNO} + \text{CO}$
 Circled numbers 1 and 7 correspond to those numbers in Table 2 and Fig. 4

Figure 4. Various NHCO_2 adduct configurations.

Figure 5. Influence of the assumed reactions (-2) and (-3). Note the vastly differing timescales of Parts a-c

- a) • Experiments from Diau et al. [7].
 — Prediction from the base model.
- b) — Reaction (-2) added to the model, using k_2 from Rohrig and Wagner[1].
- (c) — Reaction (-3) added to the model, using k_3 from Rohrig and Wagner[1].

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Supplementary Material

Table 1S. Cartesian coordinates (in units of 10^{-10} m) for the adducts and transition states shown in Figs. 3 and 4, derived at the B3LYP/6-311G(d,p) level of theory.

Adduct 1

O	0.423735	1.023949	-0.002243
C	-0.252081	-0.102344	-0.073629
O	-1.327968	-0.526842	-0.299395
N	1.079946	-0.414523	0.229386
H	1.186730	-0.461132	1.249177

Adduct 2

O	0.873794	-0.847756	0.000001
C	-0.031814	0.044898	0.000011
O	-1.332666	-0.146654	-0.000010
N	0.807449	0.997082	-0.000005
H	-1.790289	0.706308	0.000043

Adduct 3

O	-1.690417	-0.141430	-0.000003
C	-0.608994	0.342021	0.000003
H	-0.342925	1.420874	0.000009
N	0.651284	-0.533474	0.000005
O	1.620155	0.174094	-0.000004

Adduct 4

H	-2.321409	0.266344	0.000023
O	-1.588330	-0.359241	-0.000002
N	-0.479245	0.512797	-0.000003
C	0.661023	0.066684	0.000000
O	1.802079	-0.172762	0.000001

Adduct 5

H	-2.363324	0.515857	0.000313
O	-1.733904	-0.214803	-0.000016
C	-0.503532	0.280876	-0.000119
N	0.639861	0.002401	0.000097
O	1.847091	-0.062437	-0.000019

Adduct 6

O	-1.165904	-0.443945	0.014385
N	-0.007038	-0.048970	-0.007660
O	1.018865	-0.717800	0.014273
C	0.167172	1.315593	-0.170178
H	0.222553	1.743194	0.845425

Adduct 7

O	1.499842	-0.511234	0.000012
N	0.610086	0.502496	-0.000037
H	0.895497	1.484941	0.000145
C	-0.607622	0.171916	-0.000014
O	-1.689888	-0.243005	0.000012

Adduct 8

H	-2.249874	-0.220076	0.001298
N	-1.291326	-0.598792	-0.000283
O	-0.588886	0.628255	0.000105
C	0.750863	0.501729	-0.000262
O	1.436883	-0.453099	0.000177

Triplet transition state for $\text{NH} + \text{CO}_2 \rightarrow \text{HNO} + \text{CO}$

H	1.902995	1.343387	0.000000
N	1.534255	0.377119	0.000000
O	0.000000	0.839439	0.000000
C	-0.863316	-0.093155	0.000000
O	-0.932861	-1.267476	0.000000

Singlet transition state for **1** $\rightarrow$ **7**

H	-1.067510	1.518587	0.239153
N	-0.659255	0.638826	-0.062195
O	-1.248492	-0.664764	0.014201
C	0.488023	0.150823	0.003235
O	1.592761	-0.197150	0.007899

Singlet transition state for **7** $\rightarrow$ HNO + CO

H	-0.986256	1.379224	0.052923
N	-0.697337	0.409446	-0.208685
O	-1.529964	-0.467646	0.063006
C	0.763749	0.271989	0.309885
O	1.690604	-0.267014	-0.119435