



Kinetics of the NH reaction with H₂ and reassessment of HNO formation from NH + CO₂, H₂O

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Abstract

The reaction of ground-state NH with H₂ has been studied in a high-temperature photochemistry (HTP) reactor. The NH($X^3\Sigma$) radicals were generated by the 2-photon 193 nm photolysis of NH₃, following the decay of the originally produced NH($A^3\Pi$) radicals. Laser-induced fluorescence on the NH($A^3\Pi-X^3\Sigma$ 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 from 23 to 39%. This result is in excellent agreement with that of Rohrig and Wagner [Proc. Combust. Inst. 25 (1994) 975] 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 rate coefficients for NH + CO₂ could not be significantly in error [Proc. Combust. Inst. 25 (1994) 975]. This, combined with models of several combustion systems, indicates that HNO + CO cannot be the products, contrary to their suggestion [Proc. Combust. Inst. 25 (1994) 975]. 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.

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Keywords: NH; HNO; High temperature; Photochemistry reactor; Propellant dark zones; Rate coefficients; Kinetics models; Ab initio calculations

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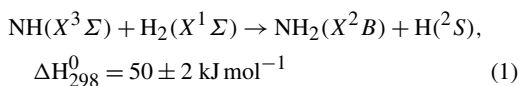
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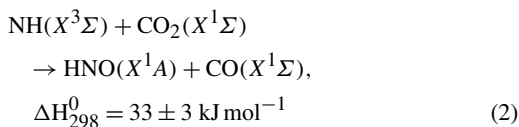
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1. Introduction

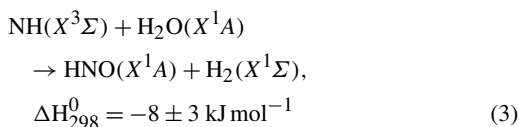
Knowledge of the kinetics of reactions of, or leading to, NH is important in combustion research. For the title reactions, apparently the only direct observations are those of Rohrig and Wagner, who studied these reactions within the 1100–2000 K temperature range behind shock waves [1]. NH in its ground 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 (1156–1685 K) = $(1.7 \pm 0.8) \times 10^{-10} \exp(-10,100 \pm 200) \text{ K}/T$, for



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



they measured k_3 (1329–1906 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 $\text{NO}/\text{CO}/\text{H}_2$ 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 H_2 in mixtures of these compounds with CO in a static reactor from 900 to 1225 K (see Appendix A). 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 CO_2 and H_2O are not those indicated by Eqs. (2) and (3). In order to decide between these possibilities we have now studied one of their reactions [1], i.e., that with H_2 , by a very different experimental technique, and have made an ab initio study of reaction (2). The results indicate that $\text{HNO} + \text{CO}$ and $\text{HNO} + \text{H}_2$ 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 Fig. 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 N_2 bath gas and a water-cooled inlet through which the photolyte NH_3 and the second reactant gas, here H_2 , 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

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