Theoretical calculations for the kinetics of the HN + NO reaction

S. Kristyan *, M.C. Lin

Department of Chemistry, Emory University, Atlanta, GA 30322, USA

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Abstract

The reaction of $^3$HN with NO producing H + N$_2$O and N$_2$ + OH has been investigated with the variational RRKM theory using existing potential energy surface data. The bimolecular constant for the loss of the reactants and those for the formation of N$_2$O and N$_2$ have been calculated and compared with experimental results. The agreement between theory and experiment appears to be satisfactory, although improvement in both areas of this important elementary reaction is desirable.

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1. Introduction

The NH radical plays a significant role in the combustion of nitramine propellants, particularly ADN, in which the reaction of NH$_x$ ($x = 1$–3) species with NO$_y$ ($y = 1, 2$) generates major chain-carriers, H and OH. The title reaction, for example, produces competitively these two species:

$$\begin{align*}
^3\text{HN} + \text{NO} & \rightarrow ^3\text{HNNO} \rightarrow \text{H} + \text{N}_2\text{O} \quad (1) \\
\overset{c}{\text{[N}_2\text{OH}]} & \rightarrow \text{N}_2 + \text{OH} \quad (2) \\
\overset{e}{\text{HNNO}( + \text{M})} & \quad (3)
\end{align*}$$

For this reaction, several research groups worldwide have attempted to determine experimentally the total reaction rate and the branching ratios for H and OH production. Values published to date vary widely [1], and no serious attempt has been reported to reconcile the data with a high-level statistical-theory calculation on the effects of temperature and pressure upon the total rate constant and product branching ratios.

In this work, we employ the variational RRKM theory to treat the barrierless NH + NO association process (a). The competitive decomposition via (b) and (c)/(d) as well as the deactivation processes (e) are determined by solving the master equation analytically. The predicted rate constant for NH + NO and the branching ratios for N$_2$O and N$_2$ production are compared with experimental values as functions of temperature and pressure.

2. Potential surface

The chemical reaction system under consideration is

$$\begin{align*}
^3\text{HN} + \text{NO} & \rightarrow [\text{HNNO}] \rightarrow \text{H} + \text{N}_2\text{O} \quad (1') \\
& \rightarrow [\text{N}_2\text{OH}] \rightarrow \text{OH} + \text{N}_2. \quad (2')
\end{align*}$$

The energetics of the stationary points along the reaction path for the HNNO system have been inves-
tigated in a number of studies [2–6]. Walch’s recent high-quality multi-reference configuration interaction (MRCI) study [5] provides the most detailed description of these energetics. A schematic diagram depicting the zero-point-corrected energetics obtained by Walch is provided in Fig. 1.

The initial reaction involves the association of NH with NO to form HNNO on the barrierless $^2\Sigma$ surface. The association on the $^2\Pi$ surface provides a more stable ($\Delta H_0 = -51.5$ kcal/mol vs. $-21.1$ kcal/mol) HNNO species but must proceed over a 3.2 kcal/mol barrier. The coupling between these two states expected to be strong since they are of the same symmetry for out-of-plane motions, we thus assume that the initially formed HNNO $^2\Sigma^+$ rapidly converts to HNNO $^2\Pi$ and that the progression onto products occurs from the $^2\Pi$ state.

The potential energies of the reactants, products, intermediates and transition states in Fig. 1 and moments of inertia and frequencies were taken from Ref. [5] for the rate estimation below, except the 97.6 kcal/mol value for $D_{\text{HH}}$ of reaction (2) which is from Ref. [2].

This information is, however, insufficient to perform a transition-state theory analysis for the entrance channel. Therefore, we have adopted the result of a detailed MRCI mapping of the barrierless part of the HN + NO ($^2\Pi$) entrance channel computed by S.J. Klippenstein using MOLPRO [7]. In this mapping, the reference configurations corresponded to a 3-electron 3-orbital CASSCF with the 3 orbitals corresponding to the 3 partially occupied orbitals of the radicals. The correlation consistent polarized valence triple zeta (cc-PVTZ) basis was used in this analysis, which involved a mapping of the reaction path and bending force constants for N–N separations ranging from 1.75 to 5.0 Å. Hindered rotor functions were then fitted to these data to provide the potential energy surface required for the subsequent variable reaction coordinate RRKM calculations [8–11].

With these data and the theories summarized in the next section, we have estimated the thermal rate constants for HN + NO as well as the branching ratios of channels (1) and (2) at high and lower pressures as functions of temperature. Experimental results are also cited below for comparison.

### 3. Rate constant calculations

Solving the nuclear Schrödinger equation exactly for a system like this is still difficult because of the great number of rovibrational states accessible during the reaction in the initial condition. Instead, we have used the well-known statistical RRKM microscopic rates for pronounced barriers and variational RRKM (VRRKM) rates [8–11] for the loose transition state using the potential surface described above. Thereafter, the master equation was solved to obtain the pressure and temperature dependence of the thermal rates. The master equation for this one-well system in Fig. 1 is

$$\frac{dx_i}{dt} = \omega \sum_j P_{ij} x_j - \omega x_i - \sum_j (k_{ij} + k_{i2} + k_{i3}) x_i,$$

where $x_i$ is the population of the $i$th rovibration energy level of HNNO adduct, $k_{ij}$ is the microscopic energy dependent rate coefficient [$k(E)$] for the $i$th level ($E = E_i$) for the three outgoing channels (b), (c) and the redissociation reaction (–a) yielding HN + NO. $P_{ij}$s are the collision energy transfer probabilities [12,13], and $\omega$ is the collision frequency (as a function of temperature and pressure). The thermal rate for the HNNO loss by one of the three exit channels is approximated by

$$k_s(P,T) = \sum_i k_{ij} x_i / \sum_i x_i.$$
There are many methods for implementing this calculation. We consider the two broadly used ones here:

(a) Calculate the VRRKM microscopic rates [8–11] for HNNO → HN + NO first and solve the master equation approximately [12,13] with the modified strong collision model [12,13]. This yields the HN + NO thermal high-pressure loss rate as a function of temperature. However, this cannot account for the outgoing channels. A more accurate method is to solve Eq. (4) analytically as described in Refs. [14,15] with the weak collision model [14,16]. The tunneling effect which is present in (1a) during the H migration was also incorporated [17]. The overall thermal rates (HN + NO → H + N₂O and HN + NO → OH + N₂) were calculated by using the method described in Ref. [18]. The angular momentum dependence of the VRRKM k(E, J) microscopic rates was averaged out [19,20] to obtain a k(E) set for calculation by Eqs. (4) and (5). This procedure yields the pressure-dependent thermal rates (the 10¹⁰ Torr pressure can be considered a high-pressure limit, and the integration was evaluated up to 70 kcal/mol above the HN + NO ZPE level with 0.25 kcal/mol step-size using Ar bath gas, 200 cm⁻¹ collision parameter which is irrelevant at high pressure and Beyer–Swinehart state count [16] up to 20 kcal/mol and Whitten–Rabinowitch thereafter). Fig. 2 shows the loss rate from HN + NO marked as M.E. Because the HN + NO ZPE level is over the two exit barriers to products, the rate to HNNO is negligible (but shows strong pressure effect), and the loss rate is practically the sum of the loss of HN + NO to products via (b) and (c)/(d), showing no pressure dependence.

(b) Along the pathway of the transition state for HNNO → HN + NO (in the 1.75–5 Å range) at each fixed N–N distance calculate the moments of inertia and extrapolate [30] the vanishing frequencies [31] among the 3M–7 real frequencies (M = number of nuclei, here 4, and there are 3 vanishing frequencies and 2 characteristic ones corresponding to the HN and NO vibrations) from the HNNO adduct 2A¹ state as νᵢ₀ exp[−α(R − R₀)], where R₀ is the N–N equilibrium distance in the 2A¹ HNNO state and νᵢ₀ are the three vanishing frequencies as i = 1, 2, 3. The potential values were used from the mapping on the 2A¹ path described above. With this, perform a variational transition state calculation (VTST) [16] by maximizing the free energy of the

![Fig. 2. High-pressure limit rate for HN + NO loss. Circles and dotted lines: experiments by (a) Mertens et al. [21] (109–790 Torr), (b) Miller et al. [22], (c) Yokoyama et al. [23] (Ar, 210–870 Torr), (d) Hansen et al. [24] (298 K, 30–700 Torr), (e) Harrison et al. [25] (1 Torr), (f) Cox et al. [26], (g) Gordon et al. [27], (h) Dean et al. [28], and (i) Kondo [29]. Theoretical curves: M.E. ~ VRRKM microscopic rates with analytical solution of the master equation using Beyer–Swinehart state count 16 up to 20 kcal/mol and Whitten–Rabinowitch thereafter. Fig. 2 shows the loss rate from HN + NO marked as M.E. Because the HN + NO ZPE level is over the two exit barriers to products, the rate to HNNO is negligible (but shows strong pressure effect), and the loss rate is practically the sum of the loss of HN + NO to products via (b) and (c)/(d), showing no pressure dependence.]

![Fig. 3. Branching ratios for the two products of the reaction HN + NO → H + N₂O or → OH + N₂ (circles = experimental points; solid line = theoretical calculation). The theoretical curve was calculated by VRRKM microscopic rates with analytical solution of the master equation like in Fig. 2 (Ar bath gas, weak collision model with 200 cm⁻¹, P = 10–15200 Torr). Experimental points are by Durant and co-workers [32,33], Quandt and Hershberger [34], Matsui and co-workers [35,36], Mertens et al. [21], and Yokoyama et al. [23].]
reaction among the chosen fixed N–N bond distance cases (or minimizing the thermal rates). This yields the high-pressure rate limit for the HN + NO loss rate, shown in Fig. 2 and marked as ‘VTST’ with a reasonable 1.0 Å⁻¹ exponent parameter for vanishing frequencies fitted to low-temperature (~300 K) rate values. The latter parameter a makes the calculation non-a-priori; however, it needs little computational time in comparison with the lengthy calculation for VRRKM rates in (a).

Fig. 2 shows the experimental loss rate [21–29] marked as a–i. Experimental results for the low-temperature range were performed at lower pressures than the high-pressure limits. However, as the calculation shows (point a above); because the TSs of two outgoing channels are below the HN + NO ZPE level, the loss rate should be pressure independent (stronger pressure dependence is expected for HN + NO → HNNO only, but this rate is much smaller than the product formation from HN + NO). The branching ratio was calculated by the method in (a) (showing no pressure but a small temperature dependence) and is shown in Fig. 3 in comparison with experimental data [21,23,32–36].

4. Summary

A comparison of the available experimental data in Figs. 2 and 3 with the theoretical ones indicates that the VRRKM theory with the master equation described above can reproduce experimental data reasonably. However, these rate estimation methods (and the accuracy of the potential surface calculations) must be improved. On the other hand, experimental results also suffer from large errors as manifested in Fig. 2, where measured rate constants with opposite slopes appear in the same temperature region. In Fig. 3, the branching ratio determined experimentally also appears to be fairly scattered. For this important reaction, both theory and experiment require further studies and improvements.

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References

[7] H.J. Werner, P.J. Knowles, MOLPRO 92, University of Sussex. MOLPRO is an ab initio program for molecular electronic structure calculations written by H.-J. Werner and P.J. Knowles with contributions from a number of other authors.