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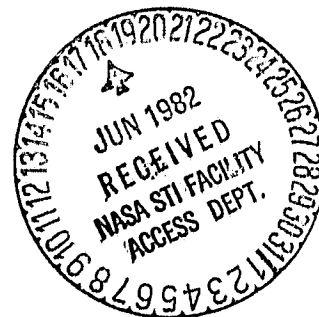
RATE CONSTANT FOR THE REACTION NH_2 + NO FROM 216 TO 480 K

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Abstract

The absolute rate constant for the reaction NH_2 + NO → products has been measured at five temperatures ranging from 216 to 480 K by the technique of flash photolysis-laser induced fluorescence (FP-LIF). NH_2 radicals were produced by the flash photolysis of ammonia and the fluorescent NH_2 photons were measured by multiscaling techniques. At each temperature, the results were independent of variations in [NO], total pressure, and flash intensity (i.e., initial [NH_2]). The results are best represented by the expression $k = (2.77 \pm 0.89) \times 10^{-7} \, T^{-1.67 \pm 0.05} \, cm^3 \, molecule^{-1} \, s^{-1}$, where the error quoted is one standard deviation. The results are compared with previous determinations using the techniques of mass spectrometry, absorption spectroscopy, laser absorption spectroscopy, and laser induced fluorescence. The implications of the results are discussed with regard to combustion, post combustion, and atmospheric chemistry. The results are also discussed theoretically.

Introduction

The reaction of NH_2 with nitric oxide,

$$NH_2 + NO \rightarrow products, \tag{1}$$
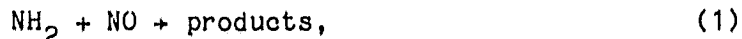
is of both laboratory and practical interest. In addition to the rate constant for reaction (1), the products of the reaction also must be known to explain the products from the photolysis of NH_3 in the presence of NO. Bamford[1] suggested that the products were exclusively H_2O and N_2. His results were corroborated by Serewicz and Noyes[2] and Srinivasan.[3] Unit quantum yield measurements for N_2 by Jayanty et al.[4] at T = 298 K and ammonia pressures of 7 torr or less, would seem to quantitatively confirm Bamford's claim. Even though this channel for reaction represents a considerable rearrangement, both products have been detected in direct experiments by Gehring et al.[5] and Silver et al.[6] Such a rearrangement very likely suggests the formation of an adduct. Nonetheless, the question of whether N_2 and H_2O formation represents the exclusive channel for reaction has been questioned in connection with

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modeling[6,7] the "Thermal De-NO$_x$" process of Lyon[8,9] and in the flame oxidation of NH$_3$.[10] Miller et al.[7] were the first to suggest that the necessary chain branching cannot occur unless reaction (1) creates radicals (i.e., either OH + N$_2$H or OH + N$_2$ + H) at about equal rates as the H$_2$O + N$_2$ channel. Other channels have been considered and rejected.[6,7] Though searches for H atoms have been attempted in direct studies of this reaction, H atoms have not been observed.[6,11] OH has, however, been observed in two studies,[6,11] and this would seem to indicate importance for OH + N$_2$H products. Silver et al.[6] suggest 0.5 ± 0.3 for this fractional branch. However, more recent experiments, reported by Wolfrum,[11] have tentatively required the branching ratio to OH + N$_2$H to be < 0.15. Thus, one of the goals of the present study is to assess whether OH is an important product from reaction (1) in agreement with Silver et al.[6] or whether only N$_2$ and H$_2$O are formed in agreement with Jayanty et al.[4] and, now, perhaps with Wolfrum and co-workers.[11]

A second goal is to determine the overall rate constant for reaction (1) over an extended range of temperature which includes that of the troposphere and stratosphere. NH$_2$ radical reactions in the atmosphere,[12] particularly that with NO, will affect both tropospheric NH$_3$ and NO distributions.

To date there have been eight determinations[5,6,13-18] of the absolute rate constant for reaction (1) at or near 298 K, with half of the studies appearing in the last three years. The agreement between these studies is not very good, the discharge flow studies yielding values about one half of those found in the flash photolysis experiments. The agreement between the three studies[6,15,18] of the temperature dependence of this rate constant is also less than satisfactory. A detailed comparison and discussion of the results at 298 K as well as the temperature dependence is reserved for the discussion section where our own results are also included.

Because of the intrinsic importance of this reaction in chemical kinetics, its importance in combustion, post combustion and atmospheric chemistry, and especially in view of the lack of agreement amongst the previous studies, we undertook the present study. Here we have employed flash photolysis coupled with laser induced fluorescence detection of NH$_2$ and have covered the temperature range 216 to 480 K. We also report experiments on the

possible formation of OH as a product of reaction (1).

Experimental

The present experiments were carried out using the flash photolysis-laser induced fluorescence technique. Our original flash photolysis-resonance fluorescence apparatus designed for detection and monitoring of O, H, Cl, Br, N, etc., was recently modified by the replacement of a larger reaction cell for the study of reactions of OH. The original apparatus and the modifications to it have been described in detail previously.[19] The considerably reduced scatter from the larger reaction cell prompted us to replace the microwave discharge lamp with a CW dye laser as source of resonance radiation in an attempt to detect NH_2. This technique has been utilized to study this reaction previously.[6,14,17,18]

The laser system consisted of an Argon ion pump laser (Spectra Physics Model No. 170) coupled with a dye laser (Spectra Physics Model No. 375). A solution of the dye Rhodamine 6G (Eastman Kodak) in ethylene glycol (1.5×10^{-3} Molar) was flowed through the dye laser. Laser power from the argon ion laser was 5 to 8 watts, while power from the dye laser averaged from 125 to 175 milliwatts. Since it was necessary to have the output wavelength correspond precisely with NH_2 absorption (570.3 nm) an etalon was used, and the following tuning technique was developed. A small fast flow discharge system containing a compact glass resonance cell was constructed and located immediately adjacent to the flash photolysis system. Pumping was provided by a large mechanical pump. The exterior of the cell was coated black and the cell was provided with Wood's horns and optical windows.

The laser beam passed through the first window into the cell while the second window was used for visual observation of the interior of the cell. A dilute solution of ammonia gas (10%) in helium flowed through the cell at a total pressure of approximately 1 torr. A microwave discharge on the gas entrance tube produced NH_2 radicals. After roughly tuning the dye laser to approximately 570.3 nm using a small monochromator, fine tuning to NH_2 absorption was accomplished by visually observing the interior of the small glass cell. When the output wavelength of the dye laser was 570.3 nm, NH_2

radicals flowing through the cell in the path of the laser beam fluoresced. A mirror was mounted between the dye laser and the flash photolysis reaction cell so that the laser beam could be deflected into the small resonance cell for periodic wavelength checks.

In order to minimize scattered light from the laser beam inside the reaction cell, sidearms were connected on opposite sides of the reaction cell and compression sealed with "O" rings to the walls of both the reaction cell and the vacuum housing. The sidearm through which the laser beam entered was sealed with a quartz window perpendicular to the laser beam, while the sidearm through which the beam exited was sealed with a quartz window at the Brewster angle to the laser beam.

At right angles to both the laser beam and the flash lamp, the fluorescent photons were collected by a quartz lens-collimator-interference filter system (577.7 nm, Ditric Optics, Inc.) onto an EMR 541 E photomultiplier tube. For minimum dark current the photomultiplier tube was operated between -20 and -30°C by passing cooled dry nitrogen gas through a coil around the tube. The fluorescent photons were recorded in repetitive flashes with a multichannel analyzer. A 175.0 nm Ditric Optics Inc. interference filter with a skewed frequency width at half maximum of -13 and +25 nm was mounted above the flash lamp to isolate the photoflash.

Fresh reaction and diffusional correction mixtures were prepared daily. We estimate that the flowing mixtures inside the reaction cell were replenished every 2-3 flashes. In the experiments, total pressures were varied by a factor of 2-4 and [NO] by a factor of five. Due to practical limits of flash lamp voltage and fluorescent signal, conditions could not be varied as greatly in the high-temperature experiments even though substantial variations were possible.

Gas handling techniques have been described in detail in previous reports from this laboratory.[19] Argon (Matheson, 99.9995%) was used as a diluent in mixtures. Ammonia (Air Products, 99.99%) was purified by bulb-to-bulb distillation at -110°C, retaining the middle third. Nitric oxide (Matheson, 99.0%) was bulb-to-bulb distilled from liquid oxygen (-183°C) and the middle

third was retained. There was no blue color present in the solid sample.

Results

Absolute rate constants for the reaction were measured under pseudo-first-order conditions, with $[NO] \gg [NH_2]$. The decay of NH_2 radicals is thus given by

$$\ell n[NH_2] = -k_{observed}\, t + \ell n[NH_2]_o. \tag{2}$$

The observed pseudo-first-order decay constant is represented by

$$k_{observed} = k_1\, [NO] + k_d \tag{3}$$

where k_1 is the bimolecular rate constant for reaction (1) and k_d is the first-order rate constant for diffusional loss of NH_2 radicals from the reaction volume viewed by the photomultiplier. Since accumulated fluorescent counts are proportional to $[NH_2]$, $k_{observed}$ and k_d are obtained by linear least squares methods from plots of the logarithm of accumulated counts against time. Typical examples of the linear plots obtained of ℓn (counts-background) against time over one and a half to two decay lifetimes are given in Figure 1 for the reaction at 480 K. Similar experiments with $[NO] = 0$ were performed to give k_d, and k_1 values were calculated from $k_{observed}$ by means of equation (3).

Rate data for the reaction of NH_2 with NO at the various experimental conditions employed in this study are presented in Table 1. The indicated errors are at the one standard deviation level as determined from repeated determinations. The rate constant decreases with increasing temperature and this temperature dependence is shown in Figure 2 as a plot of k vs T. A linear least squares treatment of the data over the temperature range 216-480 K yields the expression $k = (2.77 \pm 0.89) \times 10^{-7}\, T^{-1.67\pm0.05}\, cm^3\, molecule^{-1}\, s^{-1}$. This expression is shown as the solid line in Fig. 2.

Discussion

The results of all determinations of the rate constant for the reaction $NH_2 + NO$ at 298 K, including the present study, are summarized in chronological order in Table II. With one exception, they are all direct determinations of the absolute rate constant based on monitoring of NH_2 using absorption spectroscopy,[13] laser absorption spectroscopy,[15,16] or laser induced fluorescence.[6,14,17,18] The single exception is the study of Gehring et al.[5] whose value for k_1 is based on fitting curves for the decay of NO and the formation of N_2 as determined by mass spectrometry.

The room temperature results fall readily into two groups. There are four previous studies employing the flash photolysis technique[14-17] which yield an average value of $k_1 = 1.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Our value of 2.1×10^{-11} cm^3 molecule^{-1} s^{-1} is consistent with this. Three studies using the discharge flow technique[5,6,18] give an average value of $k_1 = 0.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The oldest study[13] using pulse radiolysis gives the highest result ($k_1 = 2.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}), but it is in better agreement with the flash photolysis studies. The difference between the results from the two techniques is well outside the 10-15% uncertainty quoted in most of the studies and appears to be real. It is probably not due to differences in total pressure since there is some overlap of the pressure ranges: 1 to 700 torr for the flash photolysis experiments and 0.6 to 4 torr for the discharge flow experiments.

The temperature dependence of the rate constant was examined in three of the previous studies.[6,15,18] A decrease in rate constant with increasing temperature was observed in each case. Lesclaux et al.[15] studied the reaction between 300 K and 500 K and obtained the result $k = 2.09 \times 10^{-8}$ $T^{-1.25}$ cm^3 molecule^{-1} s^{-1}. Over the temperature range 210-503 K, the data of Hack et al.[18] can be represented by $k = 4.5 \times 10^{-7}$ $T^{-1.85}$ cm^3 molecule^{-1} s^{-1}. Silver et al.[6] covered the unusually large temperature range of 294 to 1215 K and find that their data over this range are best represented by the empirical equation $k = 4.38 \times 10^{-5}$ $T^{-2.30}$ exp($-684/T$) cm^3 molecule^{-1} s^{-1}. Our result for the range 216 to 480 K is $k = 2.77 \times 10^{-7}$ $T^{-1.67}$ cm^3 molecule^{-1} s^{-1}. All of these results are compared graphically in Figure 3 over the 200-500 K range. Since the data base of Silver et al. include only two temperature points in this interval, the individual values of k are given in the figure.

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For all of the other studies, the data are represented by lines given by the corresponding expression quoted above. Our results are clearly in closest agreement with those of Lesclaux et al.[15] The results of Hack et al.[18] show a temperature dependence similar to ours but are lower by a factor ranging from 1.5 near 200 K to 1.9 near 500 K. This closely parallels the factor of two differences noted above between the flash photolysis and discharge flow studies at 298 K. The temperature dependence given by Silver et al.[6] in this range is much smaller than that found in the other three studies. We do note that a high temperature extrapolation of the present result would agree with the measurements of Silver et al.[6] between 600-1215 K.

Although the product channel yielding N_2 and H_2O is generally considered to represent the most important channel for reaction (1), several additional reaction channels have been considered. Most prominent among these are the following exothermic processes:
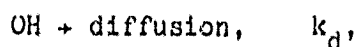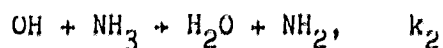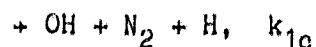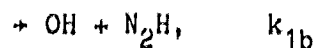
$$NH_2 + NO \rightarrow N_2 + H_2O^* \tag{1a}$$

$$\rightarrow N_2H + OH \tag{1b}$$

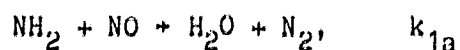$$\rightarrow N_2 + H + OH \tag{1c}$$

Evidence for process (1a) was obtained by Gehring et al.[5] and, more recently, by Wolfrum et al.[11] who detected infrared emission between 1 and 3 μ. They attributed this emission to vibrationally excited H_2O. Gehring et al.[5] also claimed detection of a small amount of the NH_2NO adduct by mass spectrometry. Silver et al.[6] report N_2 and H_2O products, but they also report OH as a product of the reaction using both resonance fluorescence and laser induced fluorescence techniques. Quantitative assessment has led this group to suggest a branching ratio for OH channels of 0.4 ± 0.1. They report negative results for the species NH_2NO, N_2H, HNO, HNNO and N_2O with mass spectrometric detection. Attempts to detect atomic hydrogen as a product of the reaction using ESR[5] and Lyman-α resonance fluorescence[6,11] have been entirely negative. Wolfrum et al.[11] recently reported experiments which confirmed the presence of OH in this system. However, these new results have tentatively been explained by a branching ratio of less than 0.15. This is a revision of an earlier

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estimate;[20] however, the revision at this stage is only tentative.

In order to investigate the relative importance of the reaction channels yielding OH radicals, the present apparatus was modified by installing an OH resonance lamp in place of the dye laser. A dilute mixture of H_2O in Ar was flowed through a microwave discharge lamp and the resultant photons were focused into the reaction cell by a lens-collimator-lens system as described previously.[19] In this particular set of room temperature experiments, signal from H_2O-Ar gas mixtures was compared to that from NH_3-NO-Ar reaction mixtures to observe the relative concentration of OH radicals in the latter case.

If the kinetics for presumed OH production and depletion are controlled by:

$$NH_2 + NO \rightarrow H_2O + N_2, \qquad k_{1a}$$

$$\rightarrow OH + N_2H, \qquad k_{1b}$$

$$\rightarrow OH + N_2 + H, \quad k_{1c}$$

$$OH + NH_3 \rightarrow H_2O + NH_2, \qquad k_2$$

$$OH \rightarrow diffusion, \qquad k_d,$$

then $(OH)_t/(NH_2)_o$ will be given by:

$$(OH)_t/(NH_2)_o = \frac{(k_{1b} + k_{1c})(NO)}{k_d + k_2(NH_3) - k_1(NO)} \left\{ e^{-k_1(NO)t} - e^{-(k_d + k_2(NH_3))t} \right\} \quad (4)$$

$(NH_2)_o$ is the initial value of (NH_2) at zero time. Experiments were performed at 20 torr total pressure and T = 298 K with (NH_3) = 50 mtorr and (NO) = 0.5 mtorr. Under these conditions $k_2(NH_3)$ = 253 s^{-1}, and OH removal by NO + M is negligible by comparison.[21] Experiments under identical conditions with (H_2O) = 60 mtorr yielded a value for k_d = 49 s^{-1}. Since k_1 is known from the present work, the exponential bracketed term and the denominator on the right

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hand side of Eq. (4) are totally specified. If $k_{1b} + k_{1c} = k_1$, then $(OH)_t/(NH_2)_0$ will attain a maximum value of 0.39 in 3.1 ms.

In order to make a valid comparison, the relationship (i.e., relative sensitivities) between $(NH_2)_0$ in the NH_3-NO-Ar experiment and the $(OH)_0$ in the H_2O-Ar experiment is necessary. Both types of experiments were performed with the 175.0 nm filter in the photoflash optical path, and with this filter the only significant photolyzing wavelength in an N_2 flashlamp is 174.4 nm where absorption coefficients for NH_3 and H_2O are respectively, about 90 and 100 $cm^{-1} atm^{-1}$ (base e and 273 K).[22] For the known optical path, $(NH_3) = 50$ mtorr, and $(H_2O) = 60$ mtorr, the ratio of absorbed light in the NH_3 case to that of H_2O is 0.8. Therefore, on the good assumption of unit quantum yields for $NH_2 + H$ and $OH + H$, experiments performed under exactly the same photoflash intensities will give nearly the same initial (H) from either source, and $(NH_2)_0$ from NH_3 will be nearly equal to $(OH)_0$ from H_2O. Thus, for $k_{1b} + k_{1c} = k_1$ (where $(OH)_t/(NH_2)_0$ attains a value of 0.39 in 3.1 ms) the maximum signal potentially obtainable in the NH_3-NO-Ar experiment would be about 30-35% of the initial OH signal from the H_2O-Ar experiment. For a photoflash energy of 45 J, the initial signal to background ratio in the H_2O-Ar experiment was 13.8 in which case a signal rising to 4.5 times the background should have been observed at 3.1 ms in the NH_3-NO-Ar case. We saw no hint of OH signal in this latter experiment indicating that the initial assumption that $k_{1b} + k_{1c} = k_1$ is incorrect. Conservatively choosing a signal to background ratio of 1.0 as the limit of detectibility, we would suggest that $k_{1b} + k_{1c} \leq 1.0/4.5\ k_1$ or the branching ratio is substantially less than 0.22.

In initial experiments with the NH_3-NO-Ar mixtures we did note substantial OH production under static conditions; however, OH did not maximize as predicted by Eq. (4). Instead it exhibited only first order decay which was entirely controlled by k_2 and k_d (reaction with NH_3 and diffusion out of the viewing zone). Further experimentation revealed that this signal came from outgassed H_2O from the vacuum line. This was established by drying research grade Ar (through a liquid N_2 trap). This dry sample of Ar was photoflashed under static conditions, and OH signal was observed indicating unambiguously that absorbed H_2O was outgassing from the vacuum line. The

effect was completely removed if Ar was continuously flowed through the cell. Thus, all subsequent experiments, particularly those described above, were performed under flowing conditions.

The present data on OH production are not in agreement with Silver et al.[6] but would seem to agree with the tentative assignment of Wolfrum et al.[11] The implications of this result to the "Thermal De-NO_x" process[8,9] and to the oxidation of NH_3[10] are ambiguous. Following Miller et al.[7], modelers of both systems[6,10] have pointed out the need for substantial branching in reaction (1) at temperatures greater than 1000 K. The present conclusion concerning radical branching (reactions (1b) and (1c)) is only valid at 298 K, and such branching may become increasingly important as temperature increases. This type of behavior clearly requires further research.

Theoretical Considerations

The present negative temperature coefficient along with chemical intuition would strongly suggest the initial formation of a singlet vibrationally excited nitrosamide adduct from NH_2 and NO doublet states since such behavior is rather common for recombination or addition type reactions. Even though the observation of the adduct has been claimed,[5] this observation has not been confirmed in later work.[6] Also since there is no pressure dependence on the observed rate constants, the hot adduct can undergo decomposition on a time scale which is short compared to the collision rate with heat bath gas. Adduct formation involves no activation energy; however, the energetics for adduct decomposition are not so straightforward.

In very recent ab initio quantum mechanical calculations Casewit and Goddard[23] give geometries and energies for the various H_2N_2O isomers. These calculations show that nitrosamide, H_2NNO, formation from NH_2 and NO is 30.6 kcal mole^{-1} exothermic. Their theoretical results are presented in Figure 4A. Unfortunately, the energies for the intermediates between the stable isomers were not calculated; however, such quantities have been calculated for the isoelectronic case, CH_3 + NO, by Adeney et al.[24] With the C-N bond energy taken at 38 kcal mole^{-1}, the relationships between the H_3CNO isomers are shown also in Figure 4B for comparison purposes with the H_2N_2O isomers. What is

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apparent in the comparison is that the stable isomers for both cases are in nearly the same relationship. The calculated 1,2 and 1,3 H shifts in the nitrosomethane case would indicate substantial activation energies for rearrangement. By analogy one would expect similar energetics for the nitrosamide case; i.e., only positive activation energy pathways for rearrangement would exist even starting with NH_2 and NO. Through the nitrosomethane analogy, Casewit and Goddard[23] suggest an overall activation energy barrier for cis and/or trans tautomer formation ranging from 0-10 kcal mole^{-1}; however, in view of the work of Adeney et al.,[24] this barrier may be underestimated. Casewit and Goddard[23] also show that subsequent formation of HN_2 + OH (reaction (1c)) would require an overall endothermicity of 12 kcal mole^{-1}. In order to respond to the implications of the "Thermal De-NO_x" results [8,9], these authors presume that (a) tautomer formation can occur and (b) tautomer subsequently reacts with radicals or with NO. We point out that (b) cannot be invoked for the conditions of the experimental rate studies. For example, in the study by Silver, et al.[6] where N_2 and H_2O are observed, the initial reactant concentrations were adjusted to such low values that subsequent radical or NO reactions with reaction (1) products were impossible. With regard to point (a), if the above mentioned analogy between nitroso-methane and nitrosamide is correct then it is difficult to rationalize tautomer formation in either case. Experimental results indicate no reaction even up to 1000 K between CH_3 and NO[25] corroborating the energetics given by Adeney, et al.[24] and shown in Fig. 4B. Since a very fast reaction does occur between NH_2 and NO (being nearly as fast as $N(^4S)$ + NO[26], and occurring in about one in 10-20 collisions), low energy pathways exist even though they have not yet been theoretically identified. Until ab initio calculations can unambiguously identify the energetics or until totally unambigious experiments are performed, the mechanism will remain speculative.

Miller, et al.[7] have already speculated on several reaction channel possibilities and conclude that rearrangement to tautomer (in agreement with Casewit and Goddard [23]) must be occurring with no energy barrier even though, as discussed above, the theoretical results probably suggest one. They further conclude that HN_2 + OH is the dominant dissociation process for the rearranged vibrationally hot tautomer even though the theoretical results indicate a 12 kcal mole^{-1} barrier. Their conclusions are based on two

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experimental facts: (a) A fast reaction does occur between NH_2 and NO, and (b) chain branching is necessary to explain the "Thermal De-NO$_x$" process. In our own speculations on this reaction, which follow, we have considered both the experimental and theoretical results.

Addition Process: Even though an activated complex calculation through a direct concerted mechanism with no energy barrier seems attractive since the theoretical temperature dependence is $T^{-1.5}$ (compared to the present $T^{-1.67}$), such calculations are always too low by 2-3 orders of magnitude. This is a direct consequence of the entropy decrease in going from reactants to a well ordered tight activated complex.
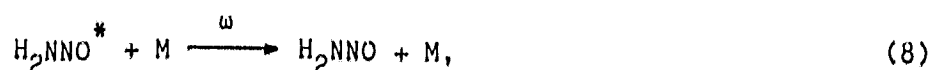
In order to obtain values which are similar to those observed, the activated complex must be taken to be loose. The loosest structure near reactants is the Lennard-Jones complex for which activated complex theory gives the same expression as collision theory,

$$k_{ad} = \frac{g^{\neq}}{g_{NO}\, g_{NH_2}} \, \sigma_{12}^2 \, \Omega_{2,2}^* (8\pi kT/\mu)^{1/2}. \tag{5}$$

The reaction coordinate has to be identified as the "vibration frequency" of the complex, and the internal modes of NH_2 and NO are taken to be the same in the reactants and complex (i.e., freely vibrating and rotating). For $g^{\neq} = 1$, $g_{NH_2} = 2$, $g_{NO} = 2(1 + \exp(-hc(121.1\ cm^{-1})/kT))$, and $\sigma_{12} = 3.085\ \text{Å}$ [27], k_{ad} can be evaluated if $\Omega_{2,2}^*$ is known. $\Omega_{2,2}^*$ is a tabulated integral and is a function of $T^* = kT/\varepsilon_{12}$ where, in the present case, $\varepsilon_{12}/k = 244\ K$ [27,28]. The results are given in Table III. Note that little temperature dependence is predicted in contrast to the data. We presume, however, that this loose complex description refers to the process of forming the nitrosamide adduct (i.e., addition). We note a strong similarity with methyl radical recombination [29] except that there are fewer degrees of freedom in the present case.

Adduct Processes: If nitrosamide adduct is formed then it is initially vibrationally hot. The subsequent fate of the hot adduct then can be

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considered from the viewpoint of unimolecular rate theory, and a partial mechanism can be written with some certainty:

$$NH_2 + NO \xrightarrow{k_{ad}} H_2NNO^*, \tag{6}$$

$$H_2NNO^* \xrightarrow{k_\epsilon^b} NH_2 + NO, \tag{7}$$

$$H_2NNO^* + M \xrightarrow{\omega} H_2NNO + M, \tag{8}$$

If these three steps entirely accounted for the fate of the hot adduct, then the observed rate constant would show pressure dependence. No pressure dependence has ever been observed. Therefore, some other process depletes H_2NNO^*,

$$H_2NNO^* \xrightarrow{k_\epsilon^f} \text{products}, \tag{9}$$

and this process has to be thermoneutral or exothermic. Endothermicity would imply a positive activation energy. Since tautomer and $HN_2 + OH$ formation are probably endothermic (see Figure 4), we suggest that the products in reaction (9) are $H_2O + N_2$. Of course this suggestion is speculative and is given only because the overall process is the most exothermic process possible and also because water and nitrogen are known to be primary products experimentally. In this event, the activated complex associated with reaction (9) has to be tight and five centered, and the barrier has to be lower lying than the hot adduct. Ab initio calculations may ultimately reveal a more satisfying explanation when the energies of the intermediates are determined.

RRK Calculations: Because of the aforementioned uncertainties in the energetics we have elected to use an RRK rather than an RRKM formulation in the present case. RRK A factors for the backward and forward nitrosamide decomposition processes can be calculated if the following are known: (a) The nitrosamide structure (We use the one determined by the ab initio calculations

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of Casewit and Goddard [23]; however, we also consider rotation about the N–N bond to be free.), (b) the two activated complexes (For the back process we use the same Lennard–Jones complex which was used for k_{ad} evaluation, and therefore, the system is microscopically reversible. For the forward dissociation we use a pyramidal structure which is based on the bond lengths of Casewit and Goddard with the N–N–O plane bisecting the NH_2 angle.), (c) the critical energies (We use the Casewit and Goddard value of 30.6 kcal mole^{-1} for the back process. We use 10 kcal mole^{-1} for the forward process.), and (d) the number of active oscillators in nitrosamide (We use one half the actual number of vibrations.). Explicit expressions for the A factor are:

$$A_b = \frac{2(2\pi kT)^{5/2}}{h^4} \cdot \frac{I_{LJ} \; I_{NO}}{(I_{NA}^{int})^{1/2}} \cdot \left(\frac{(I_1 I_2 I_3)_{NH_2}}{(I_1 I_2 I_3)_{NA}}\right)^{1/2}, \qquad (10)$$

and

$$A_f = \left(\frac{kT}{8\pi^3}\right)^{1/2} \cdot \frac{1}{(I_{NA}^{int})^{1/2}} \cdot \left(\frac{(I_1 I_2 I_3)_{\neq}}{(I_1 I_2 I_3)_{NA}}\right)^{1/2}, \qquad (11)$$

where the I's refer to moments of inertia for LJ, $\neq$, NA, and NO, which are the Lennard–Jones complex, the tight five center complex, nitrosamide, and nitric oxide, respectively. Also all vibrational partition functions are taken as unity. The calculated A factors are listed in Table III. The implications of the high rate constant which requires a loose activated complex (Lennard–Jones complex) between reactants and NA, in turn dictates (as in methyl radical recombination) a high RRK (or for that matter, RRKM) A factor for the back process. Conversely, for the forward dissociation path for which the root of the moment ratio in Eq. (11) is nearly one, the computed A factors are 2–3 orders of magnitude lower. The RRK activation function, k_ε^b, and k_ε^f values can now be evaluated, and this is done in Fig. 5A for T=216 K and 480 K.

k_1 can now be predicted since

$$k_1 = k_{ad} \int_{\epsilon_0}^{\infty} \frac{(k_\epsilon^f + \omega)}{(k_\epsilon^b + k_\epsilon^f + \omega)} \, f(\epsilon) \, d\epsilon. \tag{12}$$

Note that with such few degrees of freedom both dissociation rate constants exceed collisional stabilization, ω, by 1-3 orders of magnitude even when $\omega = 10^{10}$ s^{-1} ($\sim$ 1 atm). Thus, no pressure dependence is expected (i.e., $\omega \simeq 0$ in eq. (12)), and $k_1 = k_{ad} \left\langle k_\epsilon^f/(k_\epsilon^b + k_\epsilon^f) \right\rangle$ where the average is taken over $f(\epsilon)$ dϵ. The results are given in Table III and are compared to the present data in Fig. 5B. The prediction is uniformly higher by $\sim$60% than the observed values but exhibits a remarkably similar T dependence, $T^{-1.73}$, compared to the present, $T^{-1.67}$.

Conclusions: The application of any form of unimolecular rate theory to any system where the energetics are unknown is always a speculative exercise. The present reaction is just another case in point, and this situation strongly reiterates the need for unambiguous experimental (dynamical) and theoretical (ab initio) studies. Critical energies for dissociations have to be known with certainty.

Even so, the present RRK description is probably qualitatively correct. Obvious uncertainties exist in the critical energy for reaction (9) and in the number of active oscillators in nitrosamide. Rigorous use of RRKM theory would remove the latter but not the former uncertainty. In the limit of equilibrium, the A factors (Eqs. (10) and (11)) will be the same for either formulation, and therefore, there is not much latitude in the relative ratio since the system dictates looseness in the backward, and tightness in the forward, dissociation process activated complexes. On the other hand, relative values of k_ϵ^b to k_ϵ^f are strongly dependent on both critical energies and the number of active oscillators, and the use of RRKM (or any other unimolecular theory) will still result in a qualitative description if critical energies are unknown.

The qualitative features that are revealed by the calculation are interesting. The addition process occurs without activation energy, and the

rate is dictated by the binary collision rate and electronic degeneracy factors, as in methyl radical recombination. The adduct lifetime is too short for collisional stabilization at usual pressures. It subsequently can only be depleted by either one of two dissociation paths, one back to reactants and the other forward to products. The forward process can involve a substantial rearrangement (entropy decrease) and still dominate if its critical energy is lower than that of the back process. In the limit, $T \rightarrow 0$ K where $f(\epsilon)$ is a delta function and $k_\epsilon^b \rightarrow 0$, k_ϵ^f is still finite (in which case $k_1 = k_{ad}$). On the other hand, as T increases, $f(\epsilon)$ becomes broader, k_ϵ^b attains value, and reaction (7) opens up and competes with the forward process, reaction (9). Then, $k_1 < k_{ad}$ since $k_1 = k_{ad} \left\langle k_\epsilon^f/(k_\epsilon^f + k_\epsilon^b) \right\rangle$. Note, however, that before T becomes too large, other dissociation precesses at higher critical energies can become important. For example, suppose the critical energy for HN_2 + OH is the adduct excess energy plus the endothermicity or 42.6 kcal mole^{-1}. If this forward dissociation process has a high RRK A factor (dotted line in Figure 5A), then it is possible to have substantial changes in product ratios. Chain branching is necessary for the "Thermal De-NO_x" process and the present description offers an explanation. However, we point out that product ratios would be expected to be strongly T dependent.

Lastly, the above discussion rather clearly defines where additional work would be desirable. Additional ab initio calculations particularly on intermediates would be useful. Accurate experimental investigations on the products of reaction (1) as a function of both temperature and pressure would be illuminating. Similar experiments of the dynamical type (molecular beam) in order to assess thresholds for products would be the most unambiguous study. Spectroscopic studies of the low temperature condensed phase type would be interesting because if the present description is correct, nitrosamide might possibly be stabilized under these conditions.

Acknowledgments

References

1. C. H. Bamford, Trans. Faraday Soc. 35, 568 (1939).

2. A. Serewicz and W. A. Noyes, Jr., J. Phys. Chem. 63, 843 (1959).

3. R. Srinivasan, J. Phys. Chem. 64, 6796 (1960).

4. R. K. M. Jayanty, R. Simonaitis and J. Heicklen, J. Phys. Chem. 80, 433 (1976).

5. M. Gehring, K. Hoyermann, H. Schacke, and J. Wolfrum, Fourteenth Symposium (International) on Combustion, 14, 99 (1973).

6. J. A. Silver, C. M. Gozewski, and C.E. Kolb, Aerodyne Research Inc. Report ARI-RR-235, November, 1980; J.A. Silver and C.E. Kolb, J. Phys. Chem., submitted.

7. J. A. Miller, M. C. Branch, and R. J. Kee, Comb. and Flame, 43, 81 (1981); see also Combustion Research Bulletin, Combustion Research Program, Basic Energy Sciences, Department of Energy, July, 1981.

8. R. K. Lyon, U. S. Patent No. 3,900,544 (August 1975).

9. R. K. Lyon, Int. J. Chem. Kin. 8, 315 (1976).

10. A. M. Dean, J. E. Hardy, and R. K. Lyon, paper F8 presented at the 15th International Symposium on Free Radicals, Nova Scotia, Canada, June, 1981.

11. J. Wolfrum, paper 4 presented at the 182nd ACS National Meeting, New York, NY, August, 1981.

12. J. C. McConnell, J. Geophys. Res. 78, 7812 (1973).

13. S. Gordon, W. Mulac and P. Nangia, J. Phys. Chem. 75, 2087 (1971).

14. G. Hancook, W. Lange, M. Lenzi and K. H. Welge, Chem. Phys. Letter, 33, 168 (1975).

15. R. Lesclaux, P. V. Khe, P. Dezauzier and J. C. Soulignac, Chem. Phys. Letters 35, 493 (1975).

16. O. M. Sarkisov, S. G. Cheskis and E. A. Sviridenkov, Isv. Akad. Navk. SSSR 27, No. 11, 2612 (1978).

17. H. Kurasawa, Thesis, Universite de Bordeaux, October 1979.

18. W. Hack, H. Schacke, M. Schroter and H. Gg. Wagner, Seventeenth Symposium (International) on Combustion, p. 505 (1979).

19. R. B. Klemm and L. J. Stief, J. Chem. Phys. 61, 4900 (1974);
    L. J. Stief, D. F. Nava, W. A. Payne, and J. V. Michael, J. Chem. Phys. 73, 2254 (1980); J. V. Michael and J. H. Lee, J. Phys. Chem. 83, 10 (1979).

20. J. Wolfrum, Eighteenth Symposium (International) on Combustion 18, (1981).

21. 'Chemical Kinetic and Photochemical Data Sheets for Atmospheric Reactions", Federal Aviation Administration, U.S. Dept. of Transportation, Report No. FAA-EE-80-17, April, 1980, ed. R. F. Hampson.

22. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, 1967.

23. C. J. Casewit and W. A. Goddard III, J. Am. Chem. Soc., accepted.

24. P. D. Adeney, W. J. Bouma, L. Radom, and W. R. Rodwell, J. Am. Chem. Soc., 102, 4069 (1980).

25. A. C. Baldwin and D. M. Golden, Chem. Phys. Lett. 55, 350 (1978).

26. J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, J. Chem. Phys. 69, 3069 (1978).

27. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, 1964.

28. L. Monchick and E. A. Mason, J. Chem. Phys., $\underline{35}$, 1676 (1961). LJ parameters for NH_2 taken to be the same as H_2O.

29. S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1968.

Table I: Rate Data for the Flash Photolysis-Resonance Fluorescence Study of the Reaction NH$_2$ + NO

T,K	(NO),mtorr	(NH$_3$),mtorr	(Ar),torr	Flash energy, J[a]	No. of expts.	$k_1/10^{-11}$ cm^3 molecule^{-1} s^{-1} [b]
480	0.50	200	10	29,33	2	0.91 ± 0.07
	1.01	200	10	29,36	2	0.87 ± 0.07
	1.57	200	10	33,36	2	1.08 ± 0.02
	2.01	200	10	33	1	1.04
	1.26	238	5	7-16	3	0.91 ± 0.03
	1.88	238	5	7-16	3	0.88 ± 0.02
	2.57	238	5	7-16	3	0.86 ± 0.01
					16	0.92 ± 0.08 [c]
371	0.50	200	10	9-25	3	1.45 ± 0.05
	1.01	200	10	9-25	3	1.37 ± 0.11
	1.57	200	10	11-29	3	1.16 ± 0.09
	2.01	200	10	22,29	2	1.25 ± 0.04
	0.38	250	5	9-25	5	1.52 ± 0.12
	0.75	250	5	9-25	3	1.57 ± 0.04
	1.57	250	5	16-29	4	1.40 ± 0.18
					23	1.40 ± 0.16 [c]
298	0.09	101	10	6-14	3	1.67 ± 0.19
	0.19	103	10	6,9	2	1.84 ± 0.02
	0.38	105	10	6-14	3	2.03 ± 0.05
	0.75	100	10	9-22	3	1.76 ± 0.12
	0.09	100	5	6,9	2	1.63 ± 0.07
	0.19	100	5	6-16	3	2.21 ± 0.35
	0.38	100	5	6-16	3	2.06 ± 0.40
	0.75	100	5	6-16	3	1.92 ± 0.26
	0.09	100	2.5	3-29	6	2.17 ± 0.44
	0.19	100	2.5	3-23	7	2.34 ± 0.20
	0.38	100	2.5	3-29	7	2.29 ± 0.12
	0.75	100	2.5	3-29	9	2.20 ± 0.21
					51	2.10 ± 0.31 [c]

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Table 1: Rate Data for the Flash Photolysis-Resonance Fluorescence Study of the Reaction $NH_2 + NO$

T,K	(NO), mtorr	(NH₃), mtorr	(Ar), torr	Flash energy, J [a]	No. of expts.	$k_1 / 10^{-11}$ cm³ molecule⁻¹ s⁻¹ [b]
.253	0.07	125	5	16	1	2.72
	0.16	125	5	6-16	3	2.75 ± 0.20
	0.31	125	5	6-16	3	2.56 ± 0.15
	0.63	125	5	16	1	2.67
	0.16	125	2.5	9,16	2	2.88 ± 0.11
	0.31	125	2.5	6-16	3	2.89 ± 0.18
	0.63	125	2.5	6-16	3	2.71 ± 0.17
					16	2.74 ± 0.18 [c]
216	0.37	100	20	19-36	3	3.11 ± 0.48
	0.75	250	20	16-29	5	2.93 ± 0.32
	0.18	50	10	14-29	3	4.08 ± 0.37
	0.38	125	10	16-29	4	3.57 ± 0.18
	0.06	100	5	6-16	3	3.60 ± 0.36
	0.13	100	5	9-25	3	3.13 ± 0.43
	0.19	63	5	11-29	3	3.35 ± 0.18
	0.25	100	5	9-25	3	3.64 ± 0.24
	0.50	100	5	16-29	3	3.18 ± 0.34
	0.06	100	2.5	6	1	3.36
	0.13	100	2.5	3-16	4	3.70 ± 0.39
	0.25	100	2.5	6-16	3	3.49 ± 0.06
	0.50	100	2.5	6-16	3	3.36 ± 0.41
					41	3.41 ± 0.42 [c]

a. Effective flash energy through a 175.0 nm interference filter.

b. Error limit is one standard deviation.

c. Average k_1 at that temperature.

Table II. Comparison of Rate Data for the Reaction $NH_2 + NO$ at 298 K

Reference	$k(cm^3 \text{ molecule}^{-1} s^{-1})$	Technique[a]
Gordon et al. (1971)[13]	2.7×10^{-11}	PR – AS
Gehring et al. (1973)[5]	$(8.3 \pm 1.7) \times 10^{-12}$	DF – MS
Hancock et al. (1975)[14]	$(2.1 \pm 0.2) \times 10^{-11}$	FP – LIF
Lesclaux et al. (1975)[15]	$(1.8 \pm 0.3) \times 10^{-11}$	FP – LA
Sarkisov et al. (1978)[16]	$(1.7 \pm 0.4) \times 10^{-11}$	FP – LA
Kurasawa (1979)[17]	2.0×10^{-11}	FP – LIF
Hack et al. (1979)[18]	$(9.7 \pm 0.6) \times 10^{-12}$	DF – LIF
Silver et al. (1981)[6]	$(9.6 \pm 1.2) \times 10^{-12}$	DF – LIF
This study	$(2.1 \pm 0.3) \times 10^{-11}$	FP – LIF

[a] PR: Pulse radiolysis; AS: absorption spectroscopy; DF: discharge flow;
MS: mass spectrometry; FP: flash photolysis; LIF: laser induced
fluorescence; LA: laser absorption.

Table III: RRK Theoretical Predictions of k_1

T	k_{ad}	Λ_b	Λ_f	k_1
K	10^{-11} cm^3 molecule^{-1}s^{-1}	10^{14}s^{-1}	10^{11}s^{-1}	10^{-11}cm^3 molecule^{-1}s^{-1}
216	5.84	4.34	7.02	5.05
253	5.60	6.44	7.60	4.32
298	5.40	9.71	8.24	3.47
371	5.24	16.8	9.20	2.36
480	5.16	32.0	10.5	1.27

Figure Captions

Fig. 1. Typical decay constants of the logarithm of NH_2 fluorescent counts minus background against time at 480 K. $O - P_T = 5$ torr, $P_{NO} = 0$, $P_{NH_3} = 238$ mtorr, $k_d = 183 \pm 11$ s^{-1}; $\square - P_T = 5$ torr, $P_{NO} = 1.88$ mtorr, $P_{NH_3} = 238$ mtorr, $k_{observed} = 522 \pm 15$ s^{-1}, $\Delta - P_T = 5$ torr, $P_{NO} = 2.51$ mtorr, $P_{NH_3} = 238$ mtorr, $k_{observed} = 622 \pm 27$ s^{-1}.

Fig. 2. Plot of the bimolecular rate constant against temperature. $\bullet$ - present data at the one standard deviation level. The linear least squares line is given by $k = (2.77 \pm 0.89) \times 10^{-7}$ $T^{-1.67 \pm 0.05}$ cm^3 molecule^{-1} s^{-1}.

Fig. 3. Plot of the logarithm of the bimolecular rate constant against logarithm of temperature. Solid line, this work; dashed line, Leselaux et al.;[15] dotted line, Hack et al.;[18] $\bullet$ - Silver et al.[6]

Fig. 4. A: Ab initio quantum mechanical estimates from Casewit and Goddard[23] of the energies of stable H_2N_2O isomers relative to the present reactants, $NH_2 + NO$.
B: Ab initio quantum mechanical estimates from Adeney, Bouma, Radom, and Rodwell[24] of the energies of stable H_3CNO isomers and intermediates relative to $CH_3 + NO$ where the C-N bond strength in nitrosomethane is taken to be 38 kcal mole^{-1}.

Fig. 5. RRK calculation for $NH_2 + NO$ at 216 and 480 K. A: $f(\varepsilon)$, k_ε^b, and k_ε^f are evaluated at both temperatures. $f(\varepsilon) = k_\varepsilon^b K(\varepsilon)/\int_{\varepsilon_o}^{\varepsilon} k_\varepsilon^b K(\varepsilon)d\varepsilon$, where $K(\varepsilon) = [\varepsilon^{n-1}/(kT)^n (n-1)!] \exp(-\varepsilon/kT)$, $n=4.5$, $k_\varepsilon^b = A_b (\varepsilon-\varepsilon_o/\varepsilon)^{n-1}$, $k_\varepsilon^f = A_f (\varepsilon-\varepsilon_o'/\varepsilon)^{n-1}$, $\varepsilon_o = 30.6$ kcal mole^{-1}, $\varepsilon_o' = 10$ kcal mole^{-1}. Dotted line is an hypothetical k_ε value for $HN_2 + OH$ production at critical energy, 42.6 kcal mole^{-1}.
B: Comparison of predicted, - - - -, with experimental, ——, values of k_1 as a function of T. Prediction is made with eq. (12).
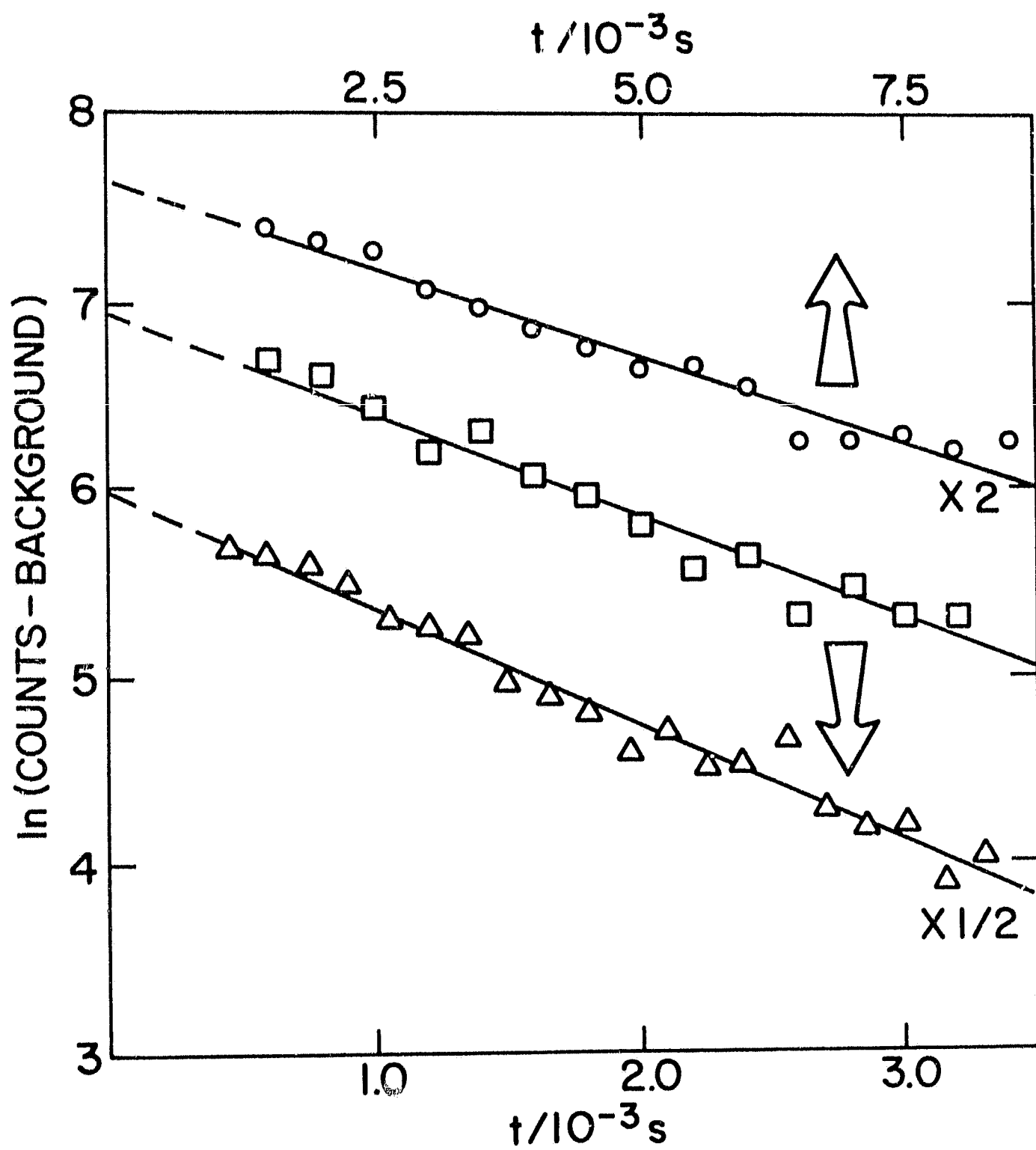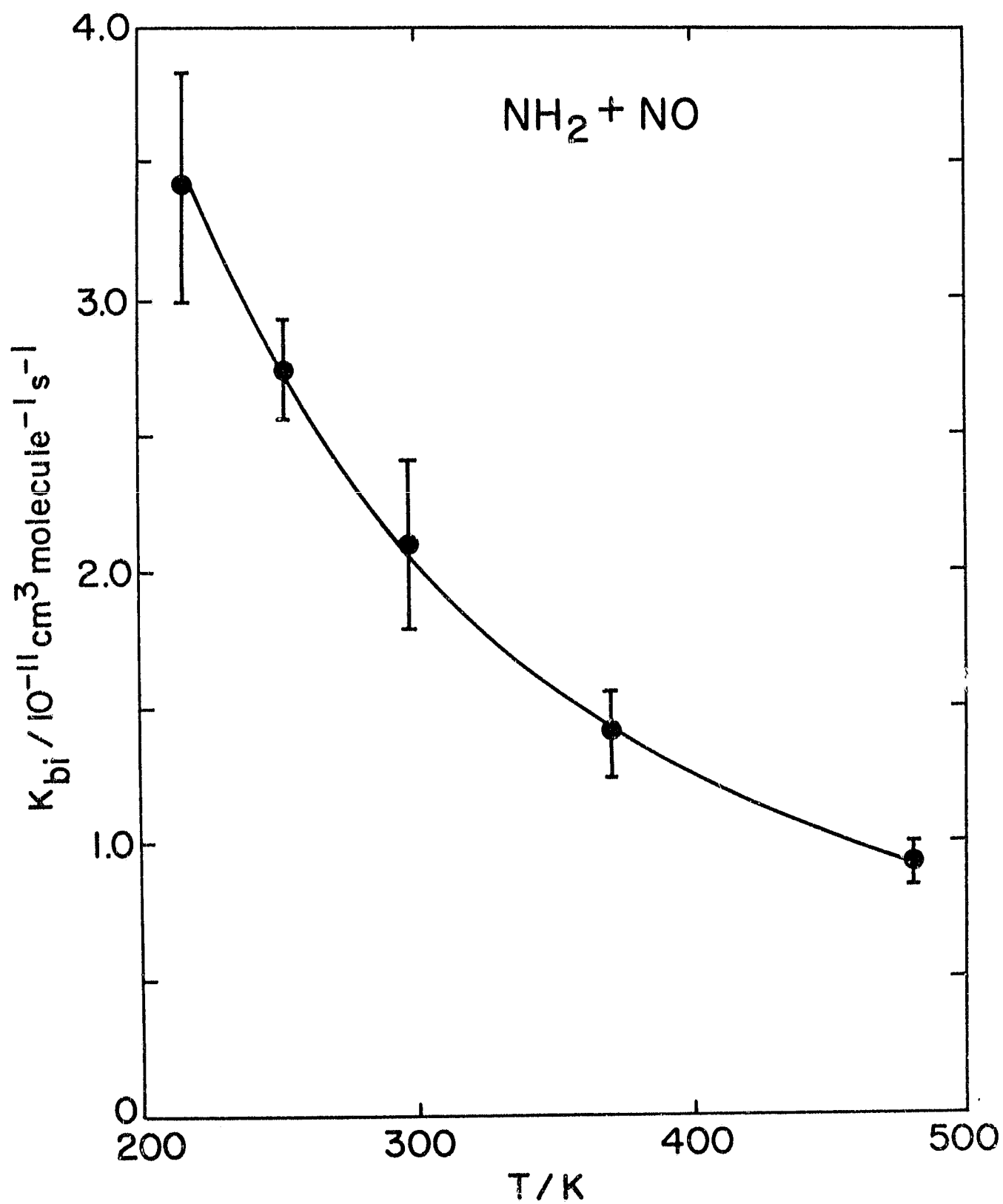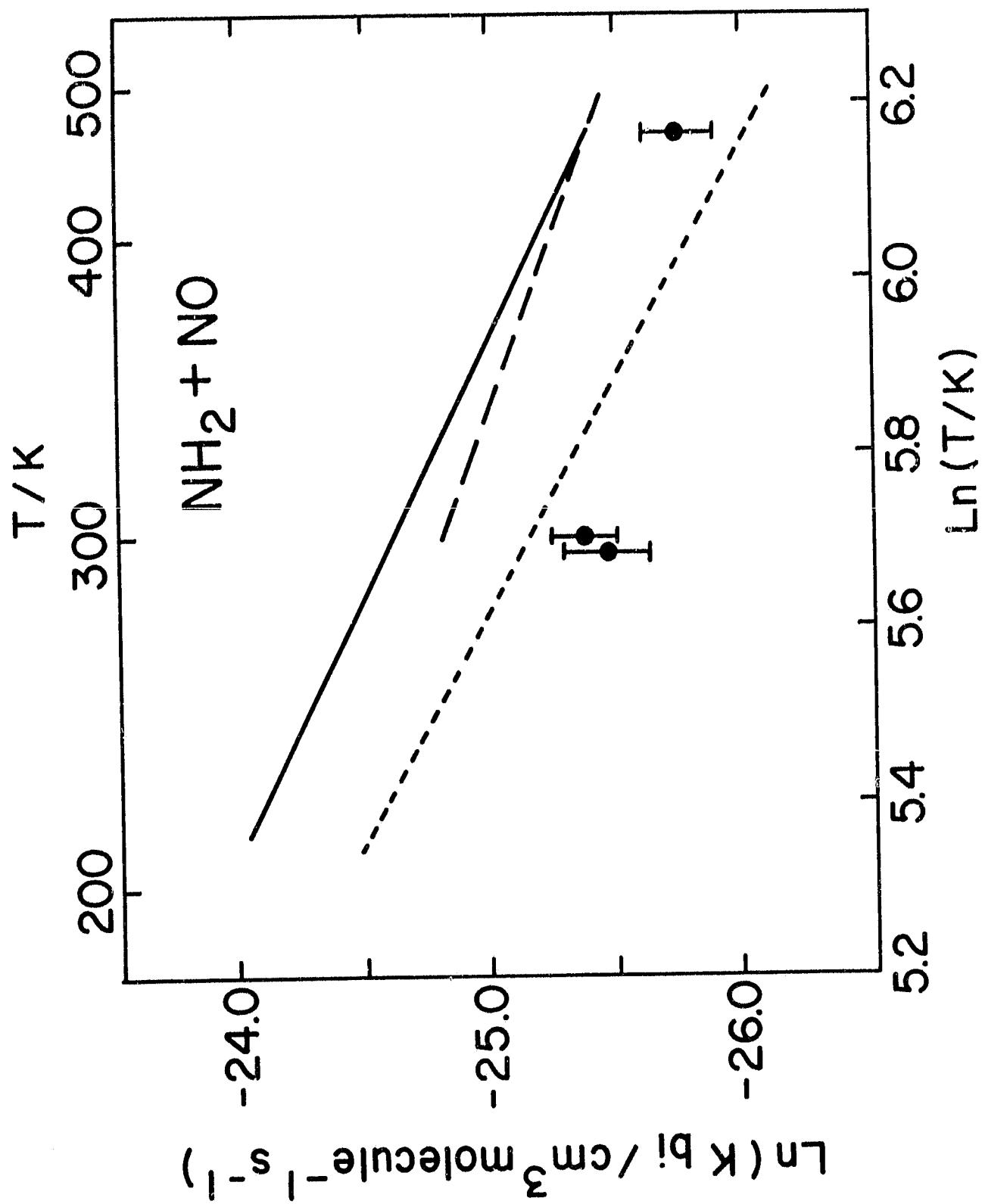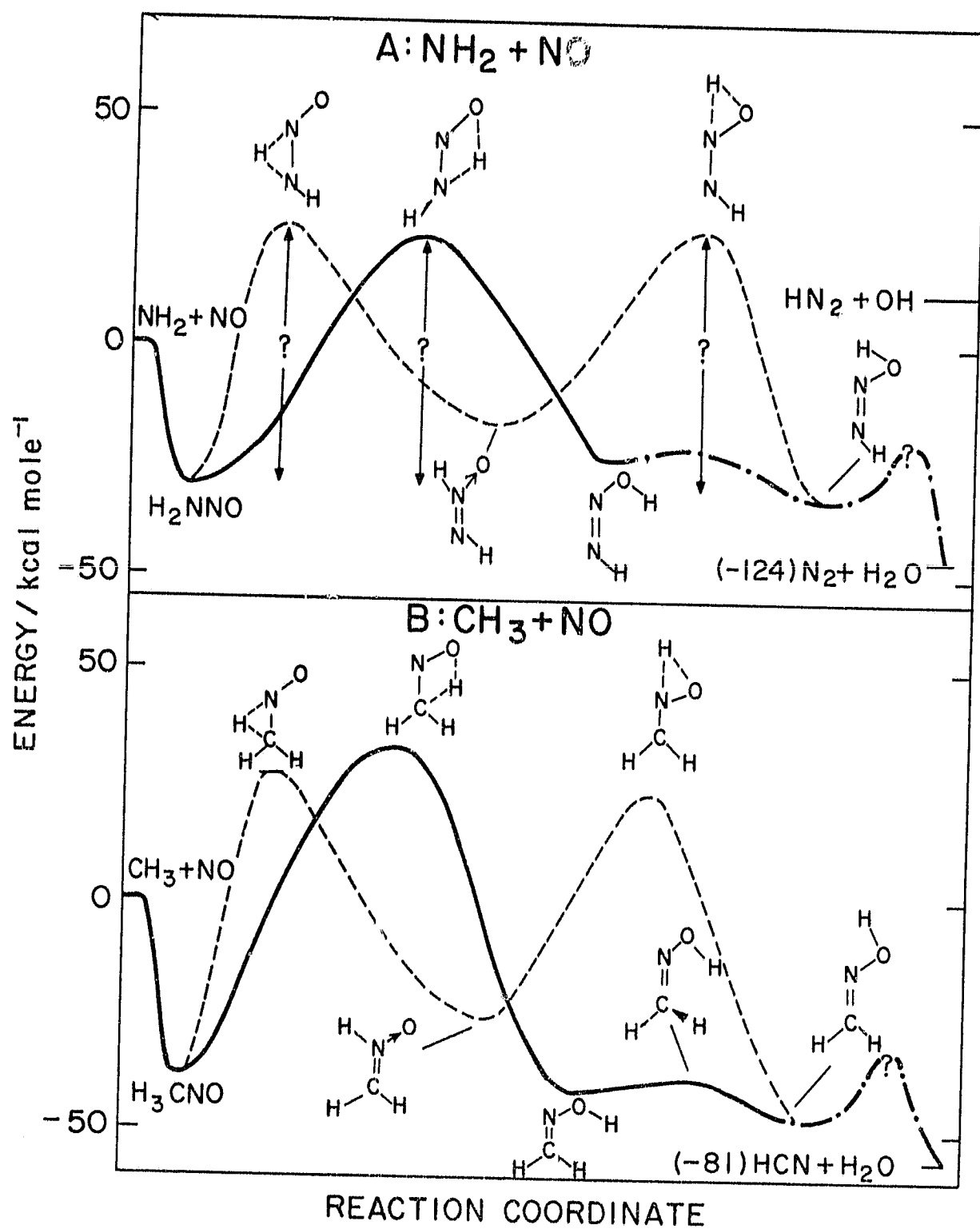
FIGURE 1

FIGURE 2

FIGURE 2

FIGURE 3

FIGURE 4

A: NH$_2$ + NO

B: CH$_3$ + NO

ENERGY / kcal mole^{-1}

REACTION COORDINATE

FIGURE 5