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Kinetics of the O(^{3}P) + N_2O Reaction. 2. Interpretation and Recommended Rate Coefficients

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The reaction O(^{3}P) + N_2O is important to models of NO_x pollutant and propellant chemistry and to the understanding of the thermal decomposition of N_2O, which has historically played a key role in the development of unimolecular reaction theory. The reaction has two important product channels: O + N_2O → NO + NO ($\Delta H_0 = -36$ kcal/mol) (R1); O + N_2O → O_2 + N_2 ($\Delta H_0 = -79$ kcal/mol) (R2). Rate coefficients of these reactions have been the subject of several reviews. However, clear reasons why many of the evaluated, nonretained data differ from recommendations have not previously been known. There has been a great deal of controversy over the rate coefficients, particularly for reaction R2. Here, the relevant data are critically evaluated using detailed chemical modeling as an important tool. The results explain many of the discrepancies. Some of the data of central importance in earlier evaluations are shown to be incorrect. Additionally, some important features of the global behavior of the mixtures studied, which had previously not been understood, are explained, and the possible effects of hypothetical H_2O contamination on N_2O shock tube studies was quantitatively investigated. It is shown that the bulk of the rate coefficient results remaining after the evaluations can be combined with the intermediate temperature results for $k_{tot} = k_1 + k_2$ from FGFAM (Fontijn, A.; Goumri, A.; Fernandez, A.; Anderson, W. R.; Meagher, N. E. *J. Phys. Chem.*, preceding paper in this issue) to obtain fitted recommendations: $k_1 = 1.52 \times 10^{-10} \exp(-13\,930/T)$ cm^3 molecule^{-1} s^{-1} (1370−4080 K); $k_2 = 6.13 \times 10^{-12} \exp(-8{,}020/T)$ cm^3 molecule^{-1} s^{-1} (1075−3340 K). Until recently, it was believed rate coefficients of the two product channels were approximately equal over a very wide temperature range. In contrast, the present study has led to the conclusion that reaction R2 dominates below, and reaction R1 above, 1840 K.

I. Introduction

The thermal decomposition and reactions of N_2O have been the subject of much study because of their importance in propellant and NO_x pollutant chemistry. The possibility of using the unimolecular reaction of N_2O as a source of O atoms for kinetics studies or as a test case for unimolecular reaction theories has also heightened interest in the reactions of N_2O. Both the thermal decomposition and combustion of N_2O depend heavily on its reaction with O atoms. The reaction is the subject of this two-part series of papers. Reasons for interest in this reaction and relevant references are presented in more detail in the introduction of the first paper in this series (FGFAM; preceding paper in this issue).[1] In FGFAM, the first measurements of the total rate coefficients at intermediate temperatures (∼1100 K) are presented. In the present paper, the voluminous literature on the reaction is critically evaluated, the data are interpreted in terms of the product channels, and rate coefficient expressions obtained from the selected data are presented.

The reaction of N_2O with O atoms has two important product channels:

$$\mathrm{O} + \mathrm{N_2O} \rightarrow \mathrm{NO} + \mathrm{NO} \qquad \Delta H_0 = -36\ \text{kcal/mol} \quad \text{(R1)}$$

$$\mathrm{O} + \mathrm{N_2O} \rightarrow \mathrm{O_2} + \mathrm{N_2} \qquad \Delta H_0 = -79\ \text{kcal/mol} \quad \text{(R2)}$$

These have been the subject of several reviews [e.g., ref 2 (BDH73), ref 3 (HS85), ref 4 (TH91), and ref 5]. Recommendations of the reviews are discussed in more detail in the Introduction of FGFAM. Briefly, early works led to a conclusion in the first review, BDH73, that the two product channels have nearly equal rate coefficients with activation energies of about 28 kcal/mol. However, a recent shock tube study[6] (DDCH92) has created some controversy. Although the authors of DDCH92 suggest no major changes are needed for k_1, they conclude the k_2 expression is very different than previously thought. In particular, they conclude that although the rate coefficients for the two channels have nearly the same magnitude at ∼2000 K, the E_a of k_2 is much smaller than previously thought; that is, k_2 was observed to be considerably smaller than k_1 above ∼2000 K and larger than k_1 below ∼2000 K. In addition to this discrepancy, results in the literature for the rate coefficients exhibit a wide spread of values. Also, modeling studies, reported herein, have shown that some of the results on which the authors of BDH73 placed heavy reliance for k_1 are invalid. The BDH73 k_1 expression has been used, either directly or indirectly, as part of the data fitted in later critical evaluations to obtain recommendations. For these reasons, it was decided that a thorough reassessment of the relevant literature was needed.

In the present work, detailed chemical computations were made to assess the quality of results in the prior studies. The techniques used, assumed chemical mechanisms, and criteria for acceptance or rejection of a given result are discussed in section II. In section III, evaluations of the literature data are presented. Finally in section IV, fitting of the retained data and discussion of the results are presented. *The major finding is that the authors of DDCH92 were essentially correct in suggesting that k_2 is smaller above ∼2000 K and larger below*

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∼2000 K than previously believed. Combination of the retained data from the literature with the intermediate temperature data for $k_{\mathrm{tot}} = k_1 + k_2$ from FGFAM leads to recommended expressions for both $k_1(T)$ and $k_2(T)$.

II. Computations and Assessment Procedures

II.a. Methods and Mechanism. Simulations of experimental data were performed using the time-dependent homogeneous reactor code SENKIN[7] (version 3.0) and one-dimensional premixed laminar flame code PREMIX[8] (version 2.55) from Sandia National Laboratories. These codes utilize the CHEMKIN-II mechanism interpreter (version 3.6) and library (version 4.9) of chemistry-oriented subroutines.[9] The CHEMKIN-II code was modified at the U.S. Army Research Laboratory (ARL) to permit the use of the falloff forms for pressure-dependent rate coefficients from the critical review of TH91. First-order sensitivities of species concentrations and, if computed, temperature to assumed rate coefficient *A* factors are obtained as an output of SENKIN and PREMIX. A postprocessor code,[10] written at ARL, was essential for computing elementary reaction rates, logarithmically normalizing the sensitivities to maximum mole fractions (see, e.g., ref 11), investigating important global chemical effects such as steady-state conditions for species and partial equilibrium for elementary reaction steps, and sorting this information.

SENKIN was used to model the shock tube, static reactor, and flow reactor experiments. Most of the static reactor and flow reactor studies utilized conditions that allow employment of SENKIN's simplest problem type, constant temperature and pressure. Some of the shock experiments used high reactant concentrations that require consideration of heat released during the reaction raising the temperature. For these, either the constant-pressure, adiabatic or constant-volume, adiabatic problem types could be used; it was typically found that the difference in results for either of these was not large. PREMIX was utilized to model the flame experiments. The thermal diffusion effect was included, and the multicomponent gas transport option was chosen, resulting in the highest level of transport theory allowed by the code. The user may choose to have CHEMKIN-based codes automatically account for reverse reactions by using thermodynamic data to compute reverse kinetic parameters. This feature was always used. Thermodynamic and transport property data were obtained from the respective Sandia databases,[12,13] except that some updates to the thermodynamics database from recent works were utilized.[14,15] Of particular importance is the use of thermodynamic data of McBride et al.[15,16] for NO. The heat of formation recommended is 0.2 kcal/mol larger than in refs 12 and 17. Though at first glance a difference this small appears trivial, the difference in reversed rate coefficients for reaction R1 is *30%* at 1000 K because NO appears as a product *twice*. These data were also used for reversing rate coefficients for reaction −R1 from the nitric oxide studies prior to including them in fits (−R indicates the reverse of reaction R).

The mechanism used for modeling the majority of the experimental data is presented in Table 1. The first 18 of the 23 reactions in this mechanism are the subset of reactions of N- and O-containing species from the detailed mechanism used in modeling propellant dark zone chemistry, described further in FGFAM, which has been developed at ARL.[18] The last five reactions, which are insignificant for dark zone modeling, were added for completeness. None of reactions R16−R23 are significant for any of the conditions encountered in the present study; however, note that rate coefficient expressions for reactions R16−R18 and R21−R23 are subject to considerable error. k_1 and, especially, k_2 were varied for testing purposes; for example, both values suggested in HS85 and preliminary values close to the final recommendations of the present study were tried, especially if k_2 was sensitive. (Situations where k_2 was found to be sensitive were curiously seldom encountered for readily measured quantities; this is one of the main difficulties in determining k_2 accurately.) A much larger version of the mechanism, discussed in more detail in FGFAM, was used for testing the possible effects of H_2O contamination for both shock tube and HTP reactor experiments, and for modeling experiments utilizing H_2/N_2O mixtures. This mechanism is too extensive to present in its entirety, but rate coefficients for some of the key reactions encountered are given in Table 2 of FGFAM. A few other important reactions will be mentioned as needed.

II.b. Evaluation Criteria. In evaluating the earlier works, several factors that could result in systematic errors were thoroughly investigated. First, the mechanism used by the original authors in analyzing their experimental data was examined. Evaluations were conducted to verify that the mechanisms used included all important ancillary reactions, with accurate rate coefficients, for the conditions of the studies. This was done primarily by comparing simulations run with the present 23 reaction mechanism to simulations run with the authors' published mechanisms used in their data analysis. Results for each were also compared to the published raw data, especially where exemplary cases were given. Second, any additional assumptions made in using the authors' given mechanism were assessed for validity. Third, when a study resulted in measurements of rate coefficients for reactions in addition to k_1 and k_2, these were checked for consistency with results from other groups. The stated purity of reagents and/or whether reagent purification was performed were additional criteria used in the assessment of data quality. It is worth noting that the results for k_{tot} presented in FGFAM were subjected to the same or more intense scrutiny as all the other studies.[1]

Temperature ranges given for the published rate coefficient expression for each publication were thoroughly assessed. In the simulations, it was discovered in some instances that the experimental parameter observed was not highly sensitive to the measured rate coefficient throughout the cited temperature range, and the range used in fitting the data for the final recommendations was adjusted accordingly. Also checked, when presented, was whether the temperature range stated in the publication matched the data taken (e.g., as shown in the tables or figures). In some cases the temperature range given for the expression vastly exceeded the temperature range of the experiments.

Additionally, some representative conditions were used to model the possible effects of H_2O contamination in the reaction mixture and of the presence of hydrogen-containing species in the mixture on experimental results where these factors seemed of concern. Possible detrimental effects of H_2O as contaminant were suggested[27] in relation to shock tube experiments on N_2O/inert gas mixtures. This possibility was examined quantitatively. Also, the experiments performed with a source of atomic hydrogen purposely included in the reaction mixture, e.g., mixtures of H_2/N_2O, were evaluated in detail, and the effects of the H atom species on the data analysis were investigated.

The results of examination of literature data are presented in section III. Section III is divided into several subsections, including five for experiments in major categories. At the beginning of those five subsections, some introductory material is presented. Then, very brief synopses of the studies performed,

TABLE 1: Mechanism Used in the Modeling of Mixtures of Species Composed of N and O Atoms[a]

no.	reaction		A	n	E_a/R	ref
R1	$O + N_2O \rightarrow NO + NO$			see the text		
R2	$O + N_2O \rightarrow O_2 + N_2$			see the text		
R3	$N_2O\ (+M) \rightarrow N_2 + O\ (+M)$	k_0	9.91E−10	0.00	28 510	19
		k_∞	1.26E+12	0.00	31 510	
	efficiencies, η_i:	/N_2 1.0/ /Ar 0.67/N_2O 5.0/ from ref 2 /O_2 0.82/ from ref 20				
R4	$N + NO \rightarrow N_2 + O$		5.43E−12	0.30	0	21
R5	$O + NO \rightarrow N + O_2$		6.31E−15	1.00	20 820	3, 4
R6	$NO + M \rightarrow N + O + M$		2.40E−09	0.00	74 700	4
	efficiencies, η_i:	/N_2 1.0/Ar 0.75/He 0.35/N_2O 2.2/ from ref 2, reverse reaction				
R7	$NO_2\ (+M) \rightarrow NO + O\ (+M)$	k_0	4.10E+04	−3.37	37644	4
		k_∞	7.60E+18	−1.27	36 883	
	efficiencies, η_i:	/N_2 1.0/ /Ar 0.71/He 0.54/N_2O 1.5/ from ref 2, reverse reaction				
R8	$NO_2 + O \rightarrow NO + O_2$		6.50E−12	0.00	−120	4
R9	$O + O + M \rightarrow O_2 + M$		5.21E−35	0.00	−900	21
R10	$N_2O + NO \rightarrow N_2 + NO_2$		7.12E−11	0.00	23 720	22
R11	$NO + NO + NO \rightarrow N_2O + NO_2$		2.95E−38	0.00	13 490	24
R12	$N_2 + M \rightarrow N + N + M$		6.10E−03	−1.60	113 200	2
R13	$NO_2 + NO_2 \rightarrow NO + NO + O_2$		2.70E−12	0.00	13 147	4
R14	$NO_2 + NO_2 \rightarrow NO + NO_3$		1.60E−14	0.73	10 530	4
R15	$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$		2.30E−13	0.00	1 600	2
R16	$N_2O + N \rightarrow N_2 + NO$		1.66E−11	0.00	10 000[b,c]	3
R17	$NO_2 + N \rightarrow N_2O + O$		8.32E−12	0.00	0[c]	3
R18	$NO_2 + N \rightarrow NO + NO$		6.61E−12	0.00	0[c]	3
R19	$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$		4.70E−35	0.00	860	2
R20	$NO_2 + O + M \rightarrow NO_3 + M$		4.10E−20	−4.08	1 242	4
R21	$NO_2 + NO \rightarrow N_2O + O_2$		1.66E−12	0.00	30 200[c]	25
R22	$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$		4.32E−12	0.00	3 870[c]	26
R23	$N + NO_2 \rightarrow N_2 + O_2$		1.66E−12	0.00	0[c]	25

[a] Units are cm^3, molecule, s, K. The parameters A, n, and E_a/R are for rate coefficient expressions in the form $k = AT^n \exp(-E_a/RT)$. For reactions involving a collider, M, the effective concentration of M is given by $C_M = [P/RT]\sum_{i=1}^{N} X_i\eta_i$ where P is pressure and X_i and η_i are the mole fraction and the efficiency, respectively, of species i. The expressions are appropriate for an N_2 collider efficiency of 1.0, adjustments to A factors having been made where necessary, except for reaction R9, which is for Ar collider. Rate coefficients of the reactions where falloff was considered, R3 and R7, are then given using $k = Fk_\infty k_L$, where $k_L = k_0C_M/(k_\infty + k_0C_M)$, $\log F = \log F_C/\{1 + [\log (k_0C_M/k_\infty)]^2\}$. For reaction R3, the simple Lindemann form, $F = 1.0$, is used.[19] For reaction R7, $F_C = 0.95 - 1.0 \times 10^{-4}\ T$, is used.[4] [b] Estimate from ref 3. [c] The rate coefficients of these reactions appear to be poorly established and should only be used with caution; some may be estimates, though this is not always clear from the source. For reaction R22, see also the discussion in BDH73.[2] From modeling results using these rate coefficients, the reactions appear to be unimportant for the present conditions.

their results, and reasons for acceptance or rejection are given, either in tables or text. More detailed discussions defending the choices then follow because the short descriptions may seem unconvincing or cryptic. However, some of the reasoning is involved, and the presentation is correspondingly lengthy. The majority of readers may be satisfied with the short comments and can proceed at these points to the following sections.

III. Evaluation of Literature Data

In this section we evaluate literature data pertaining to the title reaction obtained under a wide variety of conditions. The new intermediate temperature results of FGFAM have already been compared to those of recent studies at similar temperatures in FGFAM. Due to the direct nature of the FGFAM measurements, it is felt those are the best available in that range for k_{tot} (or k_2, which dominates the reaction at intermediate temperatures; see later). The other measurements will not be considered further here.

IIIa. Studies Containing NO in the Initial Reaction Mixture. *General Comments and Products of NO + NO Reaction*. There have been many experimental studies on NO gas mixtures which resulted in kinetic measurements for the elementary NO + NO reaction.[28−37] The studies currently available on NO utilized pure NO, or mixtures of NO with inert gas, O_2, N_2, or NO_2. These include static reactor, flow reactor, and shock tube experiments (see the following subsections). There is a large spread in results for k_{-1}; see Figure 1. In Figure 1, the reaction NO + NO is assumed to yield primarily O + N_2O, independent of the authors assuming this or the $O_2 + N_2$ channel dominates. Note also the results from refs 28−31 have been divided by the stoichiometric factor of 2 to bring them into conformity with the modern convention; that is, the rate of depletion of [NO] by reaction −R1 is $-2k_{-1}[NO]^2$. In the following subsections, studies at high NO concentration and then dilute studies are considered. It will be shown that the results of four studies, refs 29 and 35−37, should be retained. As can be seen in Figure 1, these are described very well with a straight-line Arrhenius expression. Prior to leaving the present subsection, however, the products of the elementary NO + NO reaction are discussed.

Most studies since the early 1970s have assumed the products of the elementary reaction NO + NO are O + N_2O; that is, the main reaction is −R1. The authors of both HS85 and TH91 tacitly assume this (in HS85, see the discussion on the reaction in the +R1 direction). However, in the 1950s, there was considerable controversy over whether the main product channel

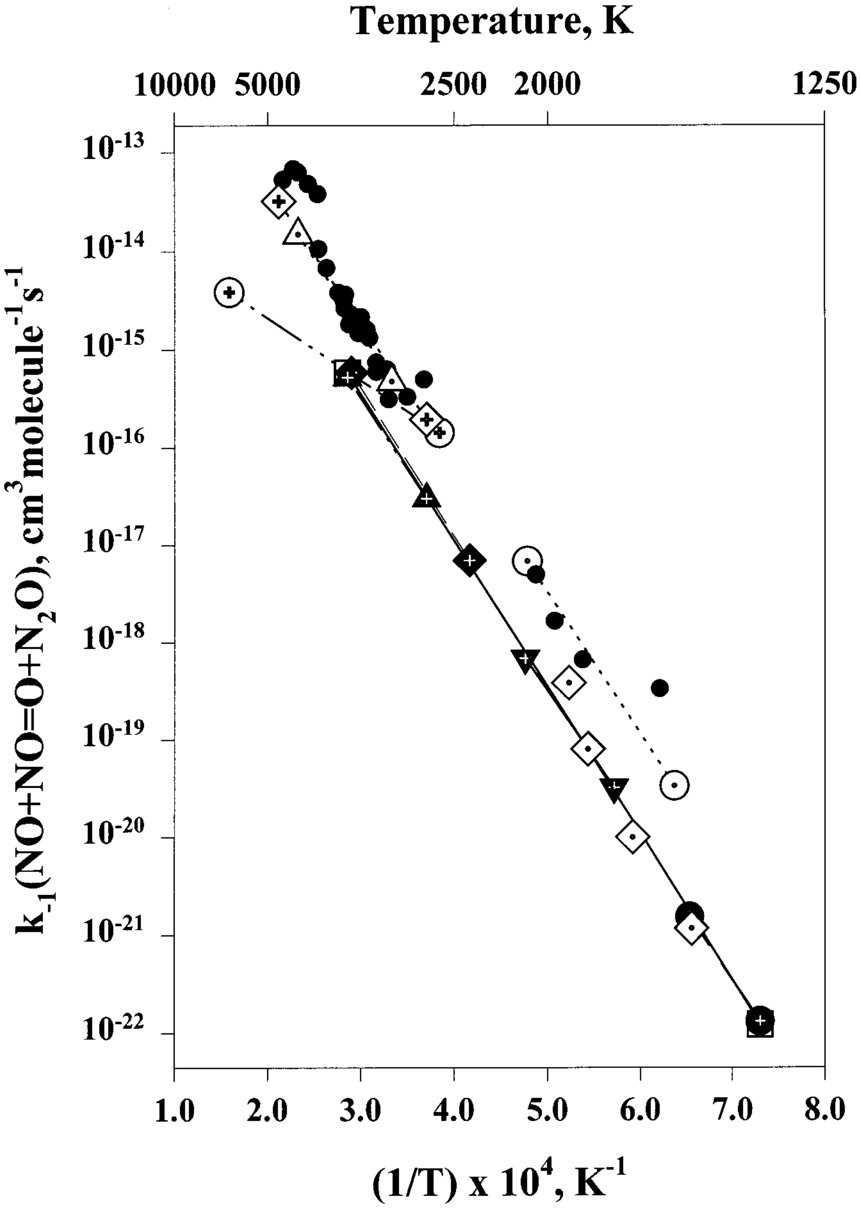

Figure 1. Arrhenius plot of rate coefficients for k_{-1}. The four results selected as best and utilized in making the present recommendations have solid symbols with white plus signs at the ends of their temperature ranges. Note that the line of the best fit to these four data sets is not the final recommendation of this work; it is presented to demonstrate the agreement of the four retained data sets over a wide temperature range. Key: ⊕—··—⊕ Myerson;[33] ◇·······◇ Trung, et al.;[34] ● Camac and Feinberg;[32] △·······△ Freedman and Daiber;[31] ◆— —◆ Theilen and Roth;[37] ▲—··—▲ Koshi and Asaba;[36] ▼———▼ McCullough, et al.;[35] ⊙·······⊙ Yuan, et al.;[30] ◇ Wise and Frech;[28] ●— — —● Kaufman, et al.;[29] □———□ least-squares fit to the four retained data sets.

is O + N_2O, or whether the reaction is instead

$$NO + NO \rightarrow O_2 + N_2 \qquad \Delta H_0 = -44 \text{ kcal/mol} \quad (R24)$$

See, e.g., the discussion in BDH73, p 254. The debate subsided in the 1960s to agreement that O + N_2O is likely the main product channel. Noteworthy in this regard were the change in position by Kaufman, who had originally favored reaction R24 (see the synopsis in BDH73), and the observation by Camac and Feinberg[32] of traces of N_2O and O atoms during shock tube studies on NO mixtures. In the present work, pertinent studies which utilized mixtures of either NO or N_2O were examined to find the most reliable rate coefficients for reactions R1 and −R1. Then, assuming the main products of the NO + NO reaction to be O + N_2O, the results for reaction −R1 were reversed using the thermodynamics. Agreement for the rate coefficients from these studies over a broad temperature range was found (see the Arrhenius diagram for reaction R1 presented later). This result would be highly unlikely if the product channel O_2 + N_2 plays a significant role. In addition, reaction R24 must proceed through a four-center transition state. This seems much less probable than reaction −R1, which can occur by a simple abstraction. A final supporting point is that recent ab initio calculations[38] have yielded a preliminary barrier height for reaction R1 of 28 kcal/mol, which corresponds to 64 kcal/mol for the reverse reaction. This agrees well with activation energies of the best results for both reactions R1 and −R1 (see later). On this basis, it seems highly likely the only important products are indeed O + N_2O. This assumption is made, allowing use of the NO experimental results in formulating recommendations.

However, before leaving the issue of products of NO + NO, it must be admitted that available works do not completely rule out the unlikely possibility that k_{-1} and k_{24} have similar magnitudes. Attempts were made to find a computed species concentration which could firmly resolve this issue by comparison with available measurements. Two sets of computations were performed across a range of conditions corresponding to the experiments on NO from the literature. The first used an assumption that O + N_2O is the only product channel; the second used the assumption that the products are evenly divided between the O + N_2O and O_2 + N_2 channels. Each case used the same total rate coefficient for NO + NO; a value was chosen which is fairly close to the reverse of the final result for k_1 recommended in the present study. The results indicated that it would be very difficult experimentally to differentiate between these two cases for *any* experimental conditions from the literature. This is especially true of the majority species NO, O_2, and N_2, because O and N_2O formed in reaction −R1 are typically rapidly converted to the final products O_2 and N_2. Thus, predicted majority species profiles for the two cases look nearly identical. The problem is also true for the trace species, O and N_2O, because their respective concentration vs time profiles predicted using the two mechanisms are approximate multiples, with ratios reflecting the assumed product ratio for the second mechanism.

To differentiate experimentally between reactions −R1 and R24 would require an absolute measurement of [O] or [N_2O], which is currently unavailable; such a measurement would be quite difficult and probably subject to debate. In addition, the modeling results for [O] and [N_2O] also depend strongly on other rate coefficients in the mechanism, e.g., k_3 and k_{10}. It seems likely the only way of resolving this issue is through ab initio calculations on reaction R24. Such calculations are presently unavailable. At present, it seems quite unlikely reaction R24 plays a significant role. Therefore, its contribution is ignored.

Studies at High NO Concentration. Four groups have performed kinetic studies on NO at high concentration.[28−30,39] Pressures used were ∼0.1−1.0 atm and temperatures ∼900 to 2100 K. In some of the works, NO was studied in pure form; also included were mixtures with O_2, N_2, NO_2, He, or CO_2. The most important of these for the present purposes are the studies on pure NO and NO/O_2 mixtures. Calculations using the mechanism in Table 1 indicate that, for representative conditions used by these authors, the overall reaction is initiated by reaction −R1. When O_2 is present and the temperature is high enough, there are also important contributions from reactions R4 and R5; additionally, the reverses of these reactions can be important for some conditions. At somewhat higher temperatures, even if pure NO is used, O_2 formed early during the decomposition can also lead to contributions by these reactions.

It was assumed in refs 28 and 29 that O and O_2 are equilibrated according to the reaction O + O = O_2, which was shown to fit the observed effect of O_2 addition on NO depletion rates. There was some debate in refs 28 and 29 over whether the O/O_2 equilibration could be due to reaction R9, with Kaufman and co-workers contending that reaction R9 is far too slow. The present computations, performed at representative conditions and using the mechanism in Table 1, indicate that although reaction R9 indeed is equilibrated, its rate is far slower than those of other reactions at these intermediate temperatures. Therefore, reaction R9 is not responsible for the O/O_2 equilibration, confirming arguments in ref 29. The calculations also show that the rates of reactions R7 and R8 are *2−3 orders of magnitude faster* than those of any other reactions, in both directions, leading to their partial equilibration during the overall reaction. Note that the sum of reactions −R7 and R8 is O + O = O_2. Therefore, these reactions, rather than reaction R9, are responsible for the O/O_2 equilibrium. The computations indicate N_2O formed in reaction −R1 is rapidly converted to N_2 via reactions R10 and R3, the former being favored at lower temperatures, the latter at higher temperatures. NO_2 formed in reaction R10 never builds up to high concentration because of rapid conversion back to NO via reaction R7 or R8. The role of reactions R4 and R5 in NO conversion at high enough T and [O_2] is very important and cannot be disregarded in the data analysis. Addition of small amounts of O_2 to NO causes an increase in the NO conversion rate due to O atoms from the O/O_2 equilibrium initiating the R5, R4 reaction sequence. However, at high enough concentration of O_2, reaction −R5 becomes important, retarding the NO conversion rate. The result is a maximum in the NO conversion rate vs [O_2] plots.[29b]

TABLE 2: Synopsis of Studies on NO at High Concentration

source	method	temp (K)	comments
Kaufman and co-workers[29]	static reactor	1170−1690	retained; *a*
Vetter[39]	flow reactor	1180−1912	discarded; *b*
Wise and Frech[28]	static reactor	872−1275	discarded; *c*
Yuan et al.[30]	static reactor	973−2087	discarded; *d*

[a] The authors' measured k_{-1} and k_5. Assumptions made regarding the mechanism, especially the O/O_2 equilibrium, are shown herein to be correct. The final result is taken from ref 29b. Some later workers have misunderstood the proper temperature range for k_{-1}. [b] The author did not consider k_{-1} in the analysis, so k_{-1} values did not result directly. The purity of the reagents was not high. Total concentrations, temperatures, and pressures of the mixtures are inconsistent. The method for conversion of NO_2 to NO within the reactor has been criticized in ref 29. k_{-1} values later resulted from the reanalysis in ref 28. [c] The authors' own experimental work yielded no results for k_{-1} because of heterogeneous reactions. They reanalyzed the ref 39 data, obtaining k_{-1} values. Besides the problems with the ref 39 data (see the preceding footnote and/or text), the authors ignored reaction −R5. This reaction is important for mixtures with high [O_2], as in ref 39. [d] The authors ignored contributions of reactions R4 and R5, and their reverses, invalidating their results for k_{-1}.

A synopsis of the four studies at high NO concentration, with brief reasons for acceptance or rejection of results presented in the footnotes, is given in Table 2. Details regarding these points form the remainder of this subsection.

In the study of Kaufman and co-workers, which is retained, NO decomposition was followed in static quartz reactors of varying size (i.e., varying surface-to-volume ratio)[29a] and in static porcelain reactors.[29b] Pure NO and NO mixtures with N_2, O_2, N_2O, or He were studied from 1170 to 1690 K. The determination of the extent of reaction involved extraction of a sample, conversion of NO or O_2 in the sample to higher nitrogen oxides via reaction with other gases, and spectrophotometric analysis. The authors excluded data below 1370 K for extraction of rate coefficients because of the observation of heterogeneous effects. Very careful purification procedures were used, especially for the NO.

The values of k_{-1} from the studies were derived from the runs on pure NO. Rate coefficients for k_{-1} were first obtained in ref 29a from measurements on pure NO in the range 1370−1530 K. In this range, the effects of the O_2 catalysis mentioned above could be eliminated. k_{-1} values were obtained using the initial [NO] depletion rates; this approach avoided the oxygen catalysis effects of O_2 formed during the reaction at the highest temperatures. Reference 29b focuses primarily on the added O_2 effects. It was mentioned that, above 1530 K, even for pure

NO, the observed reaction rates are above those computed on the basis of extrapolation of the rate coefficient expression from the prior work. The result was presumably due to O_2 catalysis; the O_2 was formed during the reaction. The work then goes on to explain the catalysis effect quantitatively, documenting measurements at temperatures from 1575 to 1690 K with added O_2. However, 30 new runs with pure NO were reported in ref 29b, made in roughly the same temperature range as the earlier study. A new rate coefficient expression is reported, which is slightly lower than that in ref 29a and is apparently from the combined studies. Extrapolated values from this k_{-1} expression were then used in the analysis of results from the runs on the NO/O_2 mixtures to obtain k_5 values for ~1500−1700 K. The k_{-1} expression does *not* extend to this higher temperature range, as some later authors have misinterpreted. The expression mentioned in ref 29b, $k = 2.0 \times 10^{-12} \exp(-32\,100\ K/T)$, 1370−1530 K, is taken as the final result of Kaufman and co-workers and used in formulating the present recommendations.

In the study of Vetter,[39] which is discarded, quartz and ceramic flow reactors were used. Mixtures of NO/O_2 were made by flowing pure NO_2 into the reactor and allowing reaction R13 to equilibrate *within the reactor*, or by making NO from the reaction of $NaNO_2$ with solutions of H_2SO_4. It should be noted that Kaufman and co-workers[29a] have criticized this and earlier flow system studies which relied on NO_2 conversion on the basis that the conversion may not have been rapid compared to residence times in the reactors. The issue is impossible to evaluate because residence times were not specified. The extent of NO conversion to N_2 for conditions with a small extent of reaction was determined from measurements of the concentrations of NO and N_2 exiting the reactor. O_2 from a steel cylinder was used in most, if not all, of the mixtures (it is unclear for which runs) and, for some, N_2 from a steel cylinder. Although some care was taken to purify the NO and NO_2 used, it is felt the method for NO (passage through a dry ice cooled tube) may not have removed all traces of H_2O from the H_2SO_4 solution. Also, the O_2 and N_2 were not of particularly high purity, which is a cause of great concern. Another difficulty is that the total quoted concentrations of NO and O_2 in Table 1, ref 39a, for the various runs do not coincide with the given temperatures and pressures. The discrepancy in some cases is up to 40% in pressure computed from the total NO + O_2 concentration and temperature as opposed to the measured pressure given in the table. The sketchy discussion does not clarify these discrepancies. It should be noted that the author, who may have understood the discrepancies, did not include the elementary NO + NO reaction in his analysis, so no k_{-1} or k_{24} rate coefficient values resulted directly from the study. For these reasons, it is concluded that the data of Vetter cannot be used.

In the work of Wise and Frech,[28] which is also discarded, a static reactor was used to study pure NO and mixtures of NO with N_2, O_2, or N_2O from 872 to 1275 K. Surface-to-volume ratio studies indicated that there are contributions from a heterogeneous reaction over nearly the entire temperature range of the authors' experimental studies. It appears this might be true even at the highest temperature used. Consequently, those results cannot be used to obtain k_{-1}, and the authors did not claim success in doing so. Along with their own data, Wise and Frech reanalyzed the data of Vetter, taking into account reactions R1, R4, and R5 and the O/O_2 equilibrium, resulting in values for k_{-1} at four temperatures. In addition to the problems mentioned in Vetter's data above, Wise and Frech ignored reaction −R5, which Kaufman and co-workers' later work shows can be important for mixtures such as Vetter's, which involved large $[O_2]$. The use of Vetter's data and failure to take reaction −R5 into account can lead to serious systematic error. It should be noted that the authors of BDH73 retained the results of Wise and Frech's reanalysis of Vetter's data in making a final recommendation.

TABLE 3: Synopsis of Studies on NO Diluted in Inert Gases

source	method	temp (K)	comments
McCullough et al.[35]	flow reactor	1750−2100	retained; *a*
Koshi and Asaba[36]	shock tube	2700−3500	retained; *a*
Theilen and Roth[37]	shock tube	2400−6200	retained; *a*, *b*
Freedman and Daiber[31]	shock tube	3000−4300	discarded; *c*
Camac and Feinberg[32]	shock tube	1610−4625	discarded; *c*
Trung et al.[34]	shock tube	2700−4700	discarded; *c*
Myerson[33]	shock tube	2600−6300	discarded; *d*

[a] All important reactions were considered. [b] The proper temperature range to use with the results is 2400−3450 K. Sensitivity to k_{-1} is seriously reduced at higher temperatures. [c] Criticized in ref 36 for failure to consider reactions R4 and R5, and for neglect of boundary layer effects. We concur that reactions R4 and R5 are substantial. This may be the primary reason for the discrepancy of these works with the retained results. [d] Disagreement with the other works resulting in k_{-1} is serious. Reactions R7, R8, and R9, which were neglected, can have substantial effects. Also, sensitivity to reaction −R1 is greatly reduced at the highest temperatures used.

Yuan et al.,[30] in another work which is discarded, studied pure NO and mixtures of NO with N_2, CO_2, or He from 973 to 2087 K. At ~1570 K, there is a pronounced change of slope in the Arrhenius plot of the observed second-order NO depletion rate coefficients, leading to the conclusion that the reaction was heterogeneous at lower temperatures. The results were analyzed assuming that only reaction −R1 occurs. This procedure is erroneous for the experiments for which the authors concluded surface effects were unimportant. Yuan et al.'s omission of the effects of reactions R4 and R5 probably accounts for the fact that k_{-1} from this study is a factor of ~10 larger than the selected values (see Figure 1). Results were not presented in enough detail to permit reanalysis.

Studies on NO Diluted in Inert Gas. Seven studies on NO mixed with inert gases were found containing rate coefficients for the NO + NO reaction.[31−37] (Note: the description of the conditions is very sketchy in ref 32, which may have actually used pure NO. That work focused primarily on N_2/O_2 mixtures, with the study and discussion of NO mixtures as a side issue. This study, like the others cited here, used higher temperatures than most of those in the previous subsection, so it is considered with the ones here.) One of the studies[35] used a ceramic flow reactor; the rest used shock tubes. Mixtures used ranged from 0.001% to 20% NO in inert gas. One study[34] used Ne, while the rest used Ar. Temperatures ranged from 1750 to 6300 K, while pressures used were generally within about a factor of 2 of atmospheric pressure. The present simulations show that the overall reaction is initiated by reaction −R1. N_2O formed at dilute conditions is primarily converted to the final product, N_2, via reaction R3. The effects of reactions R4 and R5 on consumption of NO are very important and cannot be ignored in the analysis. Also, at higher temperatures and under more dilute conditions, reactions R6 and −R9 can become very important. At high enough combined dilution and temperature, reaction R6 dominates initiation and sensitivity to reaction −R1 is lost.

A synopsis of the seven studies involving NO/inert gas mixtures, with brief reasons for acceptance or rejection of results in the footnotes, is given in Table 3. Details regarding these points form the remainder of this subsection.

The flow reactor study of McCullough et al.,[35] which is retained, utilized mixtures of 0.01−5% NO in Ar and obtained measurements in the range 1750−2100 K for k_{-1}. [NO] was measured via chemiluminescence. The results were restricted to the upper end of the temperature range used and the higher concentrations, where surface effects were determined to be negligible. The authors used a nine-reaction mechanism for data analysis. The present simulations using the Table 1 mechanism indicate all important ancillary reactions were considered.

Koshi and Asaba[36] performed incident shock measurements over the range 2700−3500 K using mixtures of 2−20% NO in Ar. Species measured included NO and O atoms. The authors point out that careful attention was paid to boundary layer effects in the analysis; they mention in earlier work they missed these effects as well as some key reactions.[40] The data were analyzed using a nine-reaction mechanism. Simulations were performed with this mechanism and compared to those using the mechanism in Table 1. The results indicate all important reactions were included. The final result[36] is retained for the present recommendations.

Thielen and Roth[37] used reflected shocks to study 0.001−1.0% NO mixtures in Ar over the 2400−6200 K temperature range. O atom and N atom concentrations were followed by atomic resonance absorption spectroscopy. Data were analyzed using an eight-reaction mechanism. Contrary to the authors' comment that they used Myerson's mechanism, their mechanism is more detailed than that of Myerson. Comparisons of simulations using Theilen and Roth's mechanism to that in Table 1 indicate all important reactions were considered. The authors were aware that, at lower concentrations used in their study, the main initiation step is reaction R6. Sensitivity to reaction −R1 is lost under those conditions, as confirmed in the present simulations. The data under these conditions were used to obtain k_6 results. For determination of k_{-1}, therefore, the data from O atom measurements and experiments with NO concentrations above 0.0025% were used.

The text of the paper makes it sound as though the k_{-1} expression obtained is valid for the entire temperature range of the study (see, e.g., the Abstract). However, the present simulations at the higher temperatures used indicate that, even for the highest concentrations, sensitivity to reaction −R1 is lost, reaction R6 becoming much more important. The presentation was detailed enough concerning the conditions that in the present study the proper upper limit for k_{-1} values from this work could be estimated as no higher than 3850 K. The authors may have been aware of this restriction, because the Arrhenius plot of their result only extends to 3450 K. The expression, with range restricted to 2400−3450 K, is plotted in Figure 1. As can be seen, it agrees extremely well with the result of Koshi and Asaba.[36] (Thielen and Roth's conclusion that their work disagreed with the Asaba group's result was based on comparison with the earlier result,[40] which has been superseded.) The result is retained and used in the present fit to obtain final recommendations.

Three shock tube studies on dilute NO mixtures from refs 31, 32, and 34, which are discarded, are discussed next. These works have previously been criticized by Koshi and Asaba[36] for failure to take into account reactions such as R4 and R5, which consume much of the available NO under these conditions, and neglect of boundary layer effects. The present simulations confirm that the neglect of reactions R4 and R5 in these studies indeed is a serious systematic error; this may be the primary reason the results from those studies are about a factor of 10 larger than those selected as best (see Figure 1).

TABLE 4: Some of the Most Sensitive Reactions Used in Modeling of the Experiments Which Involved H_2/N_2O Mixtures[a]

no.	reaction	A	n	E_a/R	ref
R25	$H + N_2O \rightarrow N_2 + OH$	3.70E−10	0.00	8 430[b]	49
		4.20E−14	0.00	2 290[b]	
R26	$NH + NO \rightarrow H + N_2O$	5.81E−10	−0.46	8	50, 51
R27	$N + NO \rightarrow N_2 + O$	5.43E−12	0.30	0	21
R28	$NO + H \rightarrow N + OH$	2.82E−10	0.00	24 560	3
R29	$OH + H_2 \rightarrow H_2O + H$	3.59E−16	1.50	1 730	52
R30	$NH + O \rightarrow NO + H$	9.12E−11	0.00	0	53
R31	$H + O_2 \rightarrow O + OH$	5.84E−08	−0.70	8 590	54

[a] Units are cm^3, molecule, s, K. The parameters A, n, and E_a/R are for rate coefficient expressions in the form $k = AT^n \exp(-E_a/RT)$. [b] For reaction R25, the rate coefficient is computed as the sum of the two exponential expressions.

The shock tube study of Myerson[33] involved the measurement of O atoms by ARAS. NO concentrations were varied from 0.1% to 10%; temperatures were varied from 2600 to 6300 K. The author determined rate coefficients for k_{-1} and k_6 using a simultaneous fitting procedure. As can be seen in Figure 1, the k_{-1} expression from this study has a much smaller slope than all the others. The activation energy to which this corresponds, 29 kcal/mol, is 7 kcal/mol less than the reaction endothermicity. For these reasons, the results have, as in prior reviews, been discarded. However, plausible reasons for the discrepancy have not previously been advanced. Sketchy information was presented regarding the pressures used, but some simulations were nonetheless performed and compared to results with the author's six-reaction mechanism. The results indicate that, depending on the concentrations, reactions R7, R8, and R9, which were neglected, can have substantial effects on the O atom profiles. These mechanism errors are probably the primary reason for the discrepancy. Also, at high enough temperatures and depending on the mixture ratio, the sensitivity of the results to reaction −R1 can be seriously reduced (see the preceding discussion of the Thielen and Roth[37] experiments). This factor could also influence the results.

III.b. Studies Containing N_2O in the Initial Reaction Mixture. Studies pertaining to the title reactions which utilized N_2O in the initial reaction mixtures will be discussed in the following three subsections. These are, respectively, works on H_2/N_2O mixtures, on N_2O at high concentration, and on N_2O diluted in inert gases. It should be mentioned that there are several works[41−45] related to the title reaction which will not be further discussed here. These early studies have been criticized and discounted in BDH73; see the discussion there regarding reaction R1.

Studies on H_2/N_2O Mixtures. There have been studies by several groups on H_2/N_2O mixtures which resulted in measurements relating to the title reaction.[46−48] These include shock tube and flame experiments. Prior to discussing the individual works, a short synopsis of rate coefficient expressions for the most sensitive H/N/O reactions used for the simulations is presented in Table 4. One reaction is worthy of special comment. It has only recently been realized that

$$H + N_2O \rightarrow NH + NO \qquad \Delta H_0 = 35 \text{ kcal/mol} \qquad (-R26)$$

has a rate coefficient expression *several orders of magnitude larger* than had been appreciated prior to about 1990 (note the reaction is written in the reverse direction in Table 4, so it will be denoted by −R26 in this text). The evidence for this point from several recent studies is quite strong.[11,51,55] As will be seen, the reaction plays a major role in NO formation during reaction

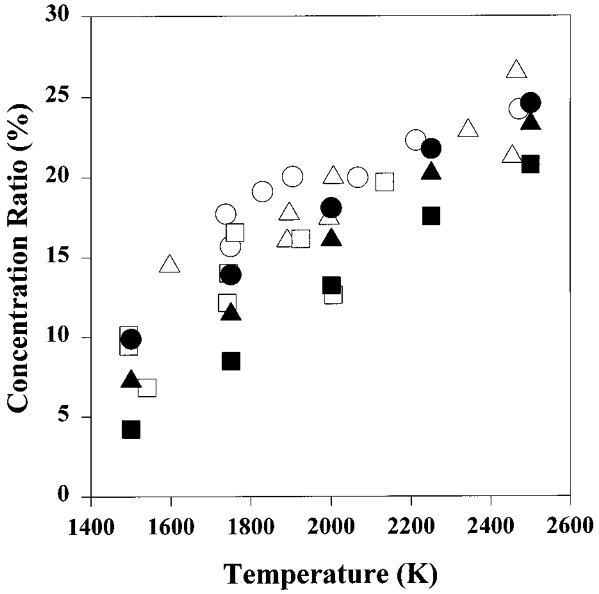

Figure 2. Comparison of computed and experimental (plateau [NO])/(initial [N_2O]) vs. temperature for the $H_2/N_2O/Ar$ shock tube experiments of Henrici and Bauer.[46] All mixtures used 1% H_2 in Ar with amounts of N_2O as indicated below. Open symbols represent experimental data, while solid symbols represent modeling results. Key: □ , ■ 1% N_2O; △ , ▲ 2% N_2O; ○ , ● 3% N_2O.

of H_2/N_2O mixtures. Since reaction −R26 has not been taken into account in any of the existing H_2/N_2O mixture studies pertaining to the title reaction, their results have been misinterpreted. k_1 results from these studies must therefore be discarded. Comparison of the present modeling results to the data from these studies shows excellent agreement is obtained using the detailed H/N/O mechanism. Details regarding these points form the remainder of this subsection.

Two groups have studied H_2/N_2O mixtures and reported rate coefficient measurements for reaction R1 using shock tubes.[46,47] The studies were performed using very similar methods and conditions, so only the results of the first of these, by Henrici and Bauer,[46] will be discussed in detail. The results of both studies for k_1 are about a factor of 10 larger than commonly accepted.[2−5] The reason for this discrepancy has not previously been understood.

Henrici and Bauer performed measurements leading to k_1 using mixtures of 1% H_2 and 1−3% N_2O in Ar for the temperature range 1700−2600 K. Profiles of OH and NO were measured. The result attributed to reaction R1 was obtained primarily from the NO measurements. [NO] was observed to increase rapidly after passage of the shocks and settle at a plateau level. The ratio of [NO] in the plateau level to initial [N_2O] was one of the key data sets produced. Rate coefficients attributed to reaction R1 were obtained by modeling this ratio using a mechanism of 14 reactions. The $H + N_2O \rightarrow NH + NO$ reaction was not included (nor was it included in ref 47).

Simulations of these data were performed in the present study using our large H/N/O mechanism. The values of k_1 and k_2 expressions were set equal to the final recommendations of the present study; it should be noted that this k_1 expression differs only modestly from the prior recommendations.[2−5] The results, shown in Figure 2, are not sensitive to k_2. Also, the results are not at all sensitive to the assumed density (from which one calculates the initial pressure for simulations) within the given range of values; this is important, because these data were not specified for the individual points. As can be seen, the agreement of the model with Henrici and Bauer's experiment is excellent toward the highest temperatures studied. The modeled [NO] may be slightly low at the lowest temperatures studied, but the agreement is still reasonable.

The important aspect of the simulations is that detailed analysis shows breakage of the N−N bond in N_2O (which is what can ultimately lead to NO formation rather than the unreactive equilibrium product N_2) is primarily due to reaction −R26 under these conditions. The final [NO] is complicated by the subsequent fate of NH thus formed. For example, NH can undergo reaction R30, resulting in formation of additional NO. Alternatively, NH can undergo reaction with OH via $NH + OH \rightarrow N + H_2O$; the N atoms thus formed then react primarily in reaction R27, which not only converts the NH to N_2, but removes an NO molecule in the process. Reaction with O_2 by $NH + O_2 \rightarrow HNO + O$, resulting in more NO being formed via $HNO + (H, OH) \rightarrow NO + (H_2, H_2O)$, is another possibility.

Sensitivity analysis reveals that, at 2000 K and 1% N_2O, the [NO] is most sensitive to reactions R25−R31 in decreasing order as given in Table 4. There is also a modest sensitivity to reaction R3, which falls between reactions R30 and R31. Reaction R1 is less sensitive than any of these, and reaction R2 is considerably below reaction R1. If instead of the present recommendation for k_1 the expression of Henrici and Bauer is substituted into the current large mechanism, the results do not agree well with experiment (not shown). Results for the 1% N_2O mixtures agree well, but for the 2% and 3% mixtures the predicted plateau [NO] to initial [N_2O] ratios are high by factors of 1.5 and 2 or more, respectively, compared to the experimental results in Figure 2, across the entire temperature range. Since experiments of refs 46 and 47 were performed under similar conditions, these comments apply equally to each. *The conclusion of the present study is that reaction −R26 and later complex NH reactions are the major source of NO in those shock tube studies rather than reaction R1 as was assumed by the authors.* Their results for the title reaction are therefore discarded.

Fenimore and Jones[48] performed experiments on several lean, low-pressure, burner-stabilized $H_2/N_2O/O_2/H_2O$ flames from which they inferred values for k_1. Temperature and stable species profiles through the flames were determined by thermocouple and quartz sampling-probe mass spectrometric measurements, respectively. O atom profiles were determined by a technique which involved isotopic labeling of a fraction of the H_2O and equilibrium assumptions, applicable to the burnt gases, for several reactions of the H/O system. The flames reached final temperatures of about 1500−2000 K. The k_1 measurements were derived from the combined temperature, N_2O, O atom, and NO profiles.

Results detailed in ref 48 for two exemplary flames were modeled in the present work using the large reaction set described earlier, with the best final values (see later) for k_1 and k_2 expressions. The computed species profiles are only modestly sensitive to changes in the k_2 expression as compared to using that of HS85. The measured temperature profiles were used as fixed input parameters in the calculations; this procedure is commonly required because heat loss processes cannot be accurately modeled.

A comparison of experimental and computed profiles for the stable species in the 1800 K flame (Figure 1 of ref 48) is shown in Figure 3. As can be seen, the agreement is excellent. The agreement is within a factor of 2 for the O atom profiles (not shown); this is quite good for such work, especially considering

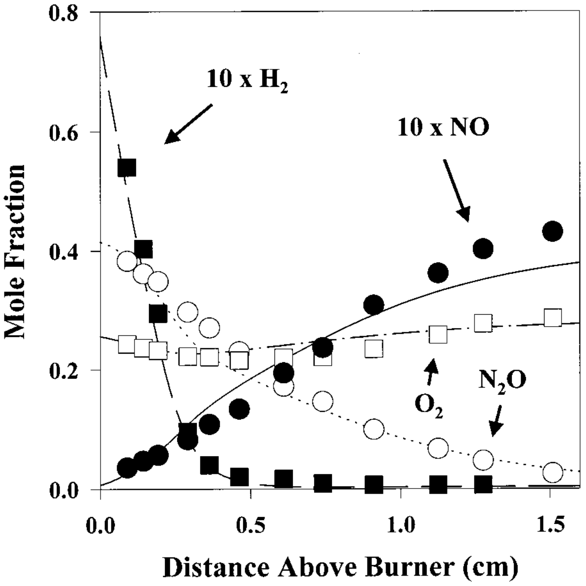

Figure 3. Comparison of computed and experimental mole fractions for the $H_2/N_2O/O_2/H_2O$ exemplary flame in Figure 1 of Fenimore and Jones.[48] Points: data from ref 48. Curves: model, present work.

the assumptions which had to be made in measuring the O atoms. The detailed analysis of reaction rates indicates that NO is not solely formed in reaction R1, as the authors of ref 48 assumed. The $H + N_2O \rightarrow NH + NO$ reaction directly contributes approximately 20% of the NO formed. Ultimately NH also contributes to NO formation by reaction R30. However, there are competing pathways for the NH which can result in its ultimate conversion to N_2 instead, so the situation is complex. (More details concerning the competing pathways under qualitatively similar situations for H_2/N_2O flames may be found in refs 11 and 56.) Not surprisingly, the computed [NO] sensitivities for reactions R1 and −R26 indicate both are very important. If reaction −R26 and the other reactions neglected in ref 48 could be taken into account in a reanalysis of the data, the results for k_1 from this work would undoubtedly be significantly altered. However, this cannot be done because results for most of the flames were not presented in sufficient detail. It seems unlikely that precision limits of the result would approach others already available in the relevant temperature range. The necessary error propagation related to precision limits of the ancillary reactions' rate coefficients and of the measured temperature profiles would probably lead to error limits in k_1 values of a factor of 2 or 3. Instead, the resulting agreement of the experiment and model is viewed as a satisfactory cross check on our current best understanding of H_2/N_2O kinetics. The k_1 measurements from the work are not used in formulating the present recommendations. It should be noted that Fenimore and Jones' k_1 expression was used as the final recommendation of BDH73. The authors of BDH73 evidently were impressed with the obvious care and ingenuity of the work, and the fact that the k_1 expression was in excellent agreement with other results highly regarded at that time. However, the present work has revealed the latter finding is fortuitous.

Study at High N_2O Concentration. The experiments on pure N_2O or N_2O mixed with several other reactants performed in static quartz reactors by Kaufman, Gerri, and Bowman[57] also have to be discarded. The most important of these for the present purposes were with pure N_2O. In the following subsection, detailed reasons for rejection of the results are given. Briefly, there are three major concerns: wall reactions, thermal equilibration at early times, and the fact that simulations show that reactions −R7 and R8, which were assumed to be negligible, have substantial effects. Details regarding these points form the remainder of this subsection.

The experiments of ref 57 covered a temperature range of 876−1030 K, with pressures from 0.013 to 0.92 atm. The $[N_2O]$ was followed by manometric methods. The [NO] was measured by the laborious procedure of stopping the reaction by expansion of the gas mixture into an evacuated absorption cell and then using spectral methods, the time evolution apparently being determined by repeated experiments of varying duration. The typical durations of the experiments were described as "20 s to several minutes". Experiments with "Vycor chips" added to the reaction vessel indicated unequivocally that wall reactions were affecting the observations.

Despite the wall reaction problem, the authors believed that they were able to properly analyze the data and obtain results bearing on the title reaction with a simple mechanism. This mechanism consisted of one-directional reactions R1, R2, R3, and −R7, the postulated reaction

$$NO_2 + N_2O \rightarrow N_2 + O_2 + NO \qquad \Delta H_0 = -6 \text{ kcal/mol} \tag{R32}$$

and the reaction of O atoms at the wall, which was assumed to be first order, i.e., $O \rightarrow (1/2)O_2$ at the wall. It was shown that at early times, where [NO] is small so that reactions −R7 and R32 supposedly could be ignored, this mechanism leads to a simple steady-state relation which defines [O] (eq "a" of ref 57). This relation was used to derive a simple equation relating the measured $[N_2O]$, the measured ratio of initial rates of formation of NO to depletion of N_2O, the unknown ratio k_2/k_1, and the unknown ratio of the wall reaction rate coefficient to k_1 (eq "b" of ref 57). By performing measurements at three pressures for each of the four temperatures used, the authors obtained an overdetermined set of three equations in the two unknown rate coefficient ratios at each temperature. Apparently, two were then used to obtain the unknown ratios with the third as a consistency check.

An elementary evaluation performed in the present work using the measured quantities (Table 1, ref 57) and resultant rate coefficient ratios (Table 7, ref 57) from Kaufman et al. reveals the results are indeed internally consistent. The ratios found for k_2/k_1 ranged from 0.67 to 0.47 between 876 and 1031 K, respectively; that is, the study concluded that the NO + NO channel occurs about twice as rapidly as the $O_2 + N_2$ channel near 1000 K. The authors then estimated the absolute value of k_1 by combining the ratio derived for k_1 to the wall rate coefficient with an estimate of the absolute wall rate coefficient using collision theory. The absolute value of k_1 derived in this way can only be regarded as very approximate, and therefore will not be given further consideration. The k_2/k_1 ratios are of more concern. The authors of BDH73 concluded that the ratio data were "probably of limited accuracy with an error limit of perhaps a factor of 2". These findings of k_2/k_1 ratios near unity at ~1000 K, coupled with other workers' similar results at higher temperatures, apparently have much to do with the BDH73 conclusion that k_1/k_2 is close to 1.0 over a wide temperature range.

Simulations of the Kaufman et al. experiments were performed in the present study to gain qualitative insights. The calculations were done using the mechanism of Table 1. The wall reaction had to be ignored because no simple way to include it in the SENKIN code is apparent. It is not clear what rate coefficient should be used in any case. Though reaction R32

TABLE 5: Synopsis of Measured Quantities in N_2O/Inert Gas Mixture Shock Tube Studies

source	species measured	method(s)[a]	inferred data	temp range (K)	comments
Monat et al.[64]	N_2O, NO	IRE	k_1, k_3	2380−4080	retained; *b*
DDCH92[6]	NO, O_2	UVA	k_1, k_2	1680−3340	retained
Lipkea et al.[61]	N_2O, NO, O_2, N_2	GC	k_1/k_2, k_3	1300−1950	discarded; *c*
Gutman et al.[58]	N_2O, O_2, N_2, NO, O	MS	k_1/k_2, k_3	1800−3500	discarded; *d*
Barton and Dove[59a]	N_2O, O_2, N_2, NO, O	MS	k_1/k_2, k_3	1800−2800	discarded; *d*
Dove et al.[59b]	none	LS	k_{tot}, k_3	2160−3590	discarded; *e*
Nip[59c]	N_2O, O_2, N_2, NO	MS	k_{tot}, k_1/k_2, k_3	2000−3250	discarded; *d*
Zaslonko et al.[63]	N_2O, NO, O	UVA, CHML	k_{tot}, k_1/k_2, k_3	1680−2500	k_1 and k_{tot} retained; *f*
Sulzmann et al.[65]	N_2O, NO	IRE, UVA	k_{tot}, k_1/k_2, k_3	1685−2560	k_1 and k_{tot} retained; *f*
Zuev and Starikovskii[27]	N_2O, NO, NO_2	IRE, UVA	k_1, upper limit k_2	1750−3300	discarded; *g*
Soloukhin[60]	N_2O	IRE	k_1, k_2, k_3	1640−3100	retained; *h*
Baber and Dean[62a]	N_2O, O	IRE, CHML	k_{tot}, k_3	1850−2535	discarded; *i*
Dean[62b]	N_2O	IRE	k_{tot}, k_3	1950−3075	discarded; *i*
Dean and Steiner[62c]	N_2O, O	IRE, CHML	k_{tot}, k_3	2100−3200	discarded; *i*

[a] MS = mass spectroscopy; LS = laser schlieren; IRE = infrared emission; GC = quenched sample gas chromatography; CHML = CO + O chemiluminescence for O-atoms; UVA = ultraviolet absorption. [b] The group's final result for k_1 is given in ref 64b. The correct temperature range for this result is given in HS85. [c] The reagents used were of poor purity. k_3 is inconsistent with the HS85 recommendation. [d] Discrepancies of k_3 results from these reflected shock studies with established results in HS85 lead to concern the temperatures may have been systematically affected by the sampling technique. Therefore, except for the notion that $k_1 \cong k_2$ at very roughly 2000 K, these results are discarded. [e] Results for k_3 compare well with those of HS85, but the Arrhenius plot for k_{tot} shows unusual curvature. k_{tot} is therefore discarded. Note the LS, incident shock technique used was very different from the methods of refs 59a,c. [f] Results of the various N_2O/inert gas shock tube studies are only sensitive to k_2 if O_2 has been measured. Therefore, the results of refs 63 and 65 for k_2 are discarded. [g] [N_2O] and [NO] were measured by IRE; NO_2 was measured by UVA. An emission attributed to NO + O was also measured. An attempt to measure [O_2] via UVA was made, but signal levels were too low. The results yield an upper limit for k_2 that is much smaller than all other studies indicate, and the implied k_{tot} expression is a factor of 2 smaller than the majority of N_2O shock studies indicate. k_{tot} is also smaller than k_1 values obtained by reversing k_{-1} results from the retained studies on NO. Reasons for the discrepancies are unclear. The authors suggested H_2O contamination may have systematically affected the other studies; simulations performed in the present work to estimate the amount needed to affect typical studies indicate this is unlikely. [h] It appears Soloukhin actually inferred k_{tot} from the N_2O data and assumed $k_1 = k_2$ to derive results. Therefore, it is assumed k_{tot} is the relevant result of the work. [i] The data were analyzed using the assumption $k_1 = k_2$, so k_{tot} is the relevant result of the work. The k_{tot} expression is lower by a factor of 2 than the majority of studies indicate; it is also smaller than k_1 values inferred by reversing k_{-1} results from the retained studies on NO. Reasons for the discrepancies are unclear.

appears plausible, to our knowledge no other studies have required the reaction; we find no clear reason to invoke it.

The simulations were tried with both the HS85 values and the final results of the present study for k_1 and k_2. The results indicate reaction rates of reactions −R7 and R8 are similar to those of the other fastest reactions involving O atoms (R1−R3), even at early times. Thus, the steady-state relation assumed in ref 57 for O atoms is drawn into question. Kaufman et al. pointed out in this early study, when k_8 was unknown, that if reaction R8 occurs, it would lead to a sharp decrease in the N_2O depletion rate by "perhaps a factor of 2" at early times. This decrease was not observed, so they concluded that reaction R8 was unimportant, and postulated that reaction *R*32 is needed. The present simulations, which used the now well-established k_8 (see refs 2 and 3), predict such a change in depletion rate would indeed occur at early times. The simulations indicate the change in the [N_2O] slope may have occurred early enough in the experiments, where the amount of N_2O consumed is quite small, that detection of the change would have been difficult. Additionally, there may have been thermal equilibration problems in the mixtures at early times. These observations, and concern about the wall effects, require discarding these k_2/k_1 results.

Studies on N_2O Diluted in Inert Gases. There have been studies by 10 groups that are pertinent to the title reaction which utilized mixtures of N_2O in inert gases.[6,27,58−65] All used shock tubes. Most used Ar as the inert diluent, though some used Kr or He. Occasionally other more reactive diluents were tried for comparison to the inert gas mixtures. Concentrations of N_2O were generally in the 0.5−5% range, with most toward the lower end of that range. Pressures generally were about 0.5−4.0 atm, though one study[27] used pressures to 23 atm. Most of the studies utilized measurement of [N_2O] as an important diagnostic. Many also included measurements of [NO], and a few measured [O] by including CO in the mixtures and following chemiluminescence of the reaction CO + O → CO_2. Only a few included measurements of [O_2]. As will be discussed, measurements of [O_2] are particularly important in the determination of k_2. Of the measured results, the following are retained in formulating recommendations for reasons discussed below: k_{tot} from Soloukhin;[60] k_1 and k_{tot} from Zaslonko et al.;[63] k_1 from Monat et al.;[64] k_1 and k_{tot} from Sulzmann et al.;[65] k_1 and k_2 from DDCH92. Some of the mass spectrometric studies[58,59a,c] indicate that $k_1 \cong k_2$ at, very roughly, 2000 K. This point was noticed in HS85 and influences both HS85 and the present recommendations. As will be seen, there is some doubt about the precision of the measured temperatures in those studies, which conclude that $k_1 = k_2$ over a broad temperature range. A synopsis of measured quantities and temperature ranges is given in Table 5. Brief reasons for our choices among the various results are given in the footnotes. Details regarding the choices form the remainder of this subsection.

Though more recent studies have generally considered most of the reactions given in Table 1, the analyses of some of the earliest ones only considered reactions R1 − R3. Representative calculations in the present work, with 2% mixtures of N_2O in Ar across the range of conditions used, generally indicate use of only reactions R1−R3 is reasonable. Future workers should also consider the possible importance of the other reactions, especially −R7, R8, and R10, as a route to O_2 formation at higher N_2O concentrations and pressures. Under the conditions generally used in the studies, the overall reaction is initiated by reaction R3. O atoms are kept in the steady state by reactions R1, R2, and R3. The N_2O is converted to N_2, O_2, and NO; concentrations of the latter three species remain at plateau levels on the time scale of shock tube experiments because the reactions converting NO to the equilibrium products N_2 and O_2 are not significant under these conditions.

Rate coefficient results for combinations of k_1, k_2, k_3, the sum $k_1 + k_2 = k_{tot}$, or the ratio k_1/k_2 have been extracted from the shapes of the various species profiles during the conversion time and/or the plateau levels (see Table 5). The slope of the k_1 Arrhenius plots has been fairly well-established in the works. Values of k_3 have been extracted in these and other studies (see reviews in refs 2−4, also refs 19, 66, and 67) and are well-established. There is disagreement by about a factor of 2 in the absolute values of k_1 from two sets of studies (see, e.g., HS85). The k_2 expressions are much more controversial.

The HS85 low-pressure k_3 recommendation is well-representative of recent results. k_3 rate coefficient expressions were a result of most, but not all, of the studies in Table 5. Comparison of k_3 values from these cases vs the HS85 recommendation is used as a check on consistency. In the data analysis of some of the studies, the k_3 expression was a fixed input parameter. The values used in this manner were examined, and there appear to be no problems resulting from the expressions utilized.

In the HS85 review, it was pointed out that the studies then available yield a strong indication that $k_1 = k_2$ at about 2000 K. All but one of the pertinent studies[27] since HS85 agree with this conclusion. Reference 27 is discussed later. First, a key point discovered by Monat et al.[64] is presented. In that work, profiles of [N_2O] and [NO] were measured spectroscopically. In the modeling, Monat et al. discovered the computed profiles were primarily sensitive to k_1 and k_3; they were much less sensitive to k_2. Therefore, the k_2 expression from BDH73 was used as an assumed parameter in the analysis, and only k_1 and k_3 values were extracted.

Computations in the present work, with the mechanism of Table 1 and either our final recommendations or the HS85 expressions for k_1 and k_2, confirm the NO sensitivity behavior. For example, for 2% mixtures of N_2O in Ar with an initial temperature of 3000 K, a change by a factor of 3 in assumed k_2 value produced only a ~15% change in the NO plateau level, which is probably similar to error limits in measured [NO]. The sensitivity of [NO] to k_1 and k_3 is much higher. For the O_2 profile, the situation regarding k_1 and k_2 is reversed; the computed profile is very sensitive to k_2 and k_3 and much less sensitive to k_1. An examination of all the computed sensitivities shows that it is difficult to find a species other than O_2 which is very sensitive to k_2; presumably N_2, though produced in reaction R2, is much less sensitive because it is also produced in reaction R3. *Thus, it is concluded that for inferring k_2, those studies which have not involved measurements of O_2 are inherently less reliable than those which have.* The same relative ordering of NO and O_2 sensitivities to k_1, k_2, and k_3 was also noted in DDCH92.

In DDCH92, NO and O_2 profiles were measured using laser absorption techniques. The results for O_2 profiles were first fitted using the N/O mechanism from HS85 but varying k_2 to obtain a fit. The k_2 expression thus obtained was then used with the NO profiles but varying k_1. Iteration could have been performed to optimize the k_1 and k_2 values, but proved unnecessary because the k_1 results matched the HS85 expression within error limits on the first trial. The results indicate k_1 predominates at high and k_2 at low temperature. The k_1 and k_2 expressions from DDCH92 are equal at 2050 K, in agreement with the observation from HS85. The Monat et al. k_1 and DDCH92 k_1 and k_2 results are therefore believed to be among the most reliable and are retained for fitting. The final result of the Monat et al. study for k_1 is found in ref 64b; the proper temperature range to use with that expression is found in HS85.

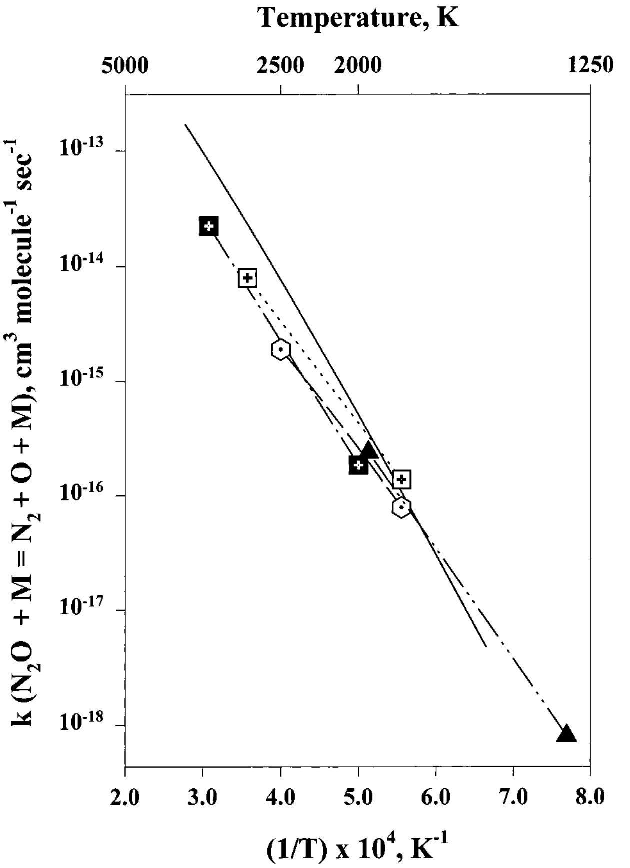

Figure 4. Arrhenius plot of results from several sources for the rate coefficient of $N_2O + M \rightarrow N_2 + O + M$. Key: ⬡— –⬡ Gutman, et al., Ar;[58] ■— –■ Nip, Kr;[59c] ⊞·······⊞ Barton and Dove, Kr;[59a] ▲—··—▲ Lipkea, et al., Kr;[61] ——— HS85, Ar.[3]

Turn to the other studies. The study of Lipkea et al.[61a] used mixtures of 2% N_2O in Kr with stated purities of only 98% and 99.7%, respectively. The N_2O was tested by gas chromatography for impurities which were found to consist primarily of "air", NO, and NO_2. These purity levels are low, and no attempt was made to increase them. In addition, results from the work for k_3 are not consistent with now well-established results such as in HS85 (see Figure 4). The HS85 k_3 recommendation is for Ar, rather than Kr, as collider, but this difference cannot account for the pronounced discrepancy in slopes. The possibility that the conditions used may have placed reaction R3 in falloff was checked during the present work using recent results on k_3 from ref 19. The conditions were in the low-pressure limit, so comparison with the HS85 k_3 is reasonable. Supply gases of similarly poor purity levels were used by Milks and Matula.[61b] For these reasons, those results were discarded.

In the mass spectrometric studies,[58,59a] k_1/k_2 was derived from the NO/O_2 concentration ratios. The experiments involved end wall sampling; hence, reflected shocks were used. In principle, these results should yield a fairly direct indication of k_1/k_2. The results from each study indicate this ratio is approximately unity for wide temperature ranges, in contrast to the result of DDCH92 (1800−2500 K from ref 58; 1960−2800 K from ref 59a). However, comparison of the results for k_3 from the two studies with the HS85 expression shows they do not agree well. Plots of low-pressure limit k_3 from refs 58 and 59a are compared to the HS85 recommendation in Figure 4. The k_3 results from refs 58 and 59a exhibit a much smaller slope than those of currently accepted expressions. The possibility that reaction R3 is in falloff under the conditions used for refs 58 and 59a was checked using k_3 results from ref 19. The conditions for both are in the low-pressure regime, so comparison with the HS85 low-pressure expression is proper. One notes the results in ref 59b for k_3 agree well with other studies and were used by the authors of HS85 in making their k_3 recommendation. However, these were obtained via a laser schlieren study on incident shocks, a technique very different from the mass spectrometric methods in ref 59a. The authors of BDH73 have suggested that the k_3 results of ref 58 are low toward the higher temperatures reported because of gas cooling by the end plate (mass spectrometer sampling region) and an incorrect understanding of the stoichiometry for the conditions used. Perhaps similar problems affect ref 59a. The idea that k_1/k_2 is near unity at, very roughly, 2000 K is strongly supported by the directly measured [NO]/[O_2] ratios in these studies. The suggestion that end plate cooling has affected the results places the temperatures specified for these ratio data in question.

The results from Nip's thesis work[59c] using the mass spectrometer were obtained with techniques similar to those of ref 59a (presumably using the identical equipment). The results were $k_1 = 2.0 \times 10^{-11} \exp(-10180K/T)$ cm^3 molecule^{-1} s^{-1} and $k_2 = 1.6 \times 10^{-10} \exp(-16340K/T)$ cm^3 molecule^{-1} s^{-1} (2000−3250 K). The corresponding k_1/k_2 ratio exhibits a downward trend vs increasing temperature, which disagrees with all other studies, and the k_1 and k_2 values imply a k_{tot} result a factor of 2 lower than the results selected as best in the present work. Nip also measured $k_3 = 5.0 \times 10^{-11} \exp(-24980K/T)$ cm^3 molecule^{-1} s^{-1} (2000−3250 K). Although this result has a slope similar to that of the HS85 expression, it is about a factor of 3 smaller (see Figure 4). Pressures used were 0.4−0.7 atm, which places reaction R3 in the low-pressure regime. Note that Nip used Kr for the diluent gas, whereas the HS85 expression is for Ar. Typically in unimolecular reactions, Kr has an efficiency similar to that of Ar; a factor of 3 lower is quite unexpected. Indeed, the measurements of Endo et al.,[68] which were also in the low-pressure regime, yielded a Kr/Ar efficiency ratio of 0.79 at 2000 K. (Note Endo et al.'s results for $k_{3,Ar}$ were among those selected for the HS85 k_3 recommendation.) One notes the fitting procedure used in HS85 gives Nip's k_1 and k_2 results little weight. The data of ref 59b for k_{tot} exhibit an unusual curvature compared to other works (see their Figure 3 and also HS85 reviews of k_1 and k_2). For these reasons, except for the result that $k_1 \cong k_2$ somewhere in the vicinity of 2000 K, none of the data of refs 58 or 59 were retained.

Two studies in which [N_2O] and [NO] were measured utilized complex analytical algebraic techniques to extract k_{tot} and k_1/k_2 values.[63,65] The result from Sulzmann et al.[65] is $k_1/k_2 = 0.92 \pm 0.08$ across the 1685−2560 K region. This would not appear to agree well with DDCH92 or the present recommendations (see later). However, the error limit reported in that work appears to be too small. Results for most of the individual points (see their Figure 3) have much larger error limits than the final result indicates. The small reported error limit in k_1/k_2 appears to be the result of averaging the 10 individual points, which may serendipitously coincide well, and of the usage of the standard deviation of the average as the error limit. The k_1/k_2 ratio of the present recommendations, given later, compares well with most of the points of ref 65 (not shown) when their individual error limits are considered. The ratio result of Zaslonko et al.[63] is $k_1/k_2 = 5.4 \exp(-4030K/T)$ (1700−2500 K). The result is the earliest found which indicates a strong upward trend in k_1/k_2 ratio with temperature. However, as mentioned earlier, studies on N_2O/inert gas mixtures confined to N_2O and NO measurements are not very sensitive to k_2; furthermore, solution of the simultaneous equations in k_{tot} and k_1/k_2 must ultimately involve differencing of two quantities of similar magnitude (k_1 or k_2 from k_{tot}). Due to this fact, studies which utilized direct [O_2] measurements to derive k_2 are to be preferred. References 63 and 65 provide an indication that k_2 has roughly the same magnitude as k_1 at high temperatures, but k_2 cannot be determined much more precisely than this by the methods used. Therefore, only the k_{tot} and k_1 values from refs 63 and 65 were retained for the present fits.

The study of Zuev and Starikovskii[27] is at variance with all the other studies in which k_2 was measured. Though the k_1 expression from that work agrees well with the HS85 recommendation, an upper limit for k_2 of $0.05k_1$ (1750−3300 K) was obtained. All the other k_2 results[6,58,59a,c,63,65] are much larger than this upper limit. Zuev and Starikovskii[27] measured [N_2O], [NO], [NO_2], and emission attributed to NO + O and analyzed their data with a detailed chemical model. They also attempted to measure [O_2], but were unsuccessful due to low signal levels. Their studies utilized mixtures of 3% N_2O in Ar with pressures from 2.5 to 23 atm. The higher pressures used are much larger than in any of the other studies. At the higher pressures used, reactions −R7 and R8 become important, complicating the data analysis.

In addition to studying N_2O/Ar mixtures, Zuev and Starikovskii also performed experiments with H_2/N_2O/Ar mixtures, investigating the effects of hydrogenous species. The experimental and modeling results led to the conclusion that N_2O/inert gas mixture chemistry is very sensitive to traces of H_2O. Further, they suggested all the other studies may be incorrect regarding k_2 because of H_2O contamination. If H_2O is present, the reactions $O + OH \rightarrow O_2 + H$ and $H + N_2O \rightarrow OH + N_2$ can speed N_2O conversion, leading to O_2 formation. The sum of these reactions, $O + N_2O \rightarrow O_2 + N_2$, could kinetically mimic reaction R2.

Zuev and Starikovskii's result that k_2 is very small and suggestion that the presence of H_2O is responsible for the much larger values from all other shock tube studies in which k_2 was measured has been investigated computationally in the present work. The present results prove that it is highly unlikely that H_2O is the cause of this major difference in reported k_2 values. The exact cause of the discrepancy is unclear, but the predominance of larger values from the other works precludes inclusion of Zuev and Starikovskii's results in formulating the final recommendation.

The [H_2O] necessary to have a significant effect was first estimated. An exemplary result is shown in Figure 5. Here, a mixture of 2% N_2O in Ar, constant pressure 2.0 atm, initial temperature 2000 K, and adiabatic conditions were assumed, and the large detailed mechanism described earlier was used. In Figure 5A, there was no H_2O in the mixture and the final k_1 and k_2 values of the present study were used. As will be seen, near 2000 K these have k_1 and k_2 approximately equal; they are similar to the HS85 recommendations for this temperature. That is, the mechanism being used for Figure 5A with no H_2O present in the modeling mixture leads to species profiles representative of those actually observed in most of the experiments of workers other than ref 27, because at ∼2000 K these k_1 and k_2 values are very similar to the results of the other experiments. Assuming Zuev and Starikovskii are correct, the k_2 expression used to produce Figure 5A is incorrect; rather, their k_2 value suggests removal of reaction R2 is more appropriate. The reaction was therefore removed and the

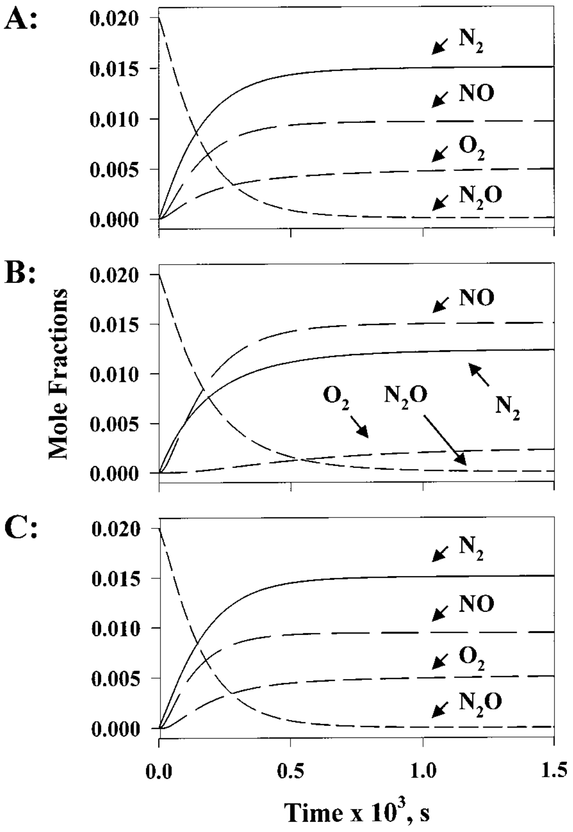

Figure 5. Simulated results of a typical N_2O/Ar shock tube experiment. The computations were performed to quantitatively estimate the effects of H_2O contamination. Conditions: 2% N_2O, initial temperature 2000 K, constant pressure 2.0 atm, adiabatic. (A) Mechanism of Table 1 using the final recommendations of the present study for k_1 and k_2; no H_2O. (b) Mechanism as in (A), except the reaction $O + N_2O \rightarrow O_2 + N_2$ has been removed; no H_2O. (C) Mechanism as in (B); 100 ppm H_2O added to the initial mixture.

calculation repeated, resulting in the profiles of Figure 5B, which are very different from the typical "experimental" observations; cf. Figure 5A. Furthermore, if $k_2 = 0$ were correct and H_2O contamination were responsible for other workers observations, it should be possible to reproduce the "experimental" profiles in Figure 5A by adding H_2O to the modeling mixtures. This was done for a variety of H_2O concentrations.

As can be seen in Figure 5C, for which the mechanism identical to that in Figure 5b was used, an excellent match to Figure 5A is obtained at about 100 ppm H_2O. Not only do the plateau concentrations of NO, N_2, and O_2 match those of Figure 5a, but even the N_2O conversion time is reduced, making agreement between parts A and C of Figure 5 excellent. Concentrations of H_2O substantially different from 100 ppm do not yield agreement with the plots of Figure 5A.

An H_2O contaminant concentration of 100 ppm may seem small, but discussions with D. F. Davidson[69] have revealed that such a value would actually be quite large; many of the following comments developed from communications with him. It has long been known in shock tube studies that H_2O contamination arises primarily from outgassing from the wall. Typically, shock tube workers strive to minimize this problem by evacuating the tube, quickly filling it with the test mixture, and rapidly thereafter performing the experiment. In experiments at the Stanford laboratory (e.g., DDCH92), the time between fill and shock is no more than a few minutes. If, for any reason, the delay between fill and experiment exceeds about 5 min, the test mixture is discarded. One to two minutes is more typical. In DDCH92, the quoted outgassing rate was 16×10^{-6} Torr/min; combining this with an assumed (abnormally long) 5 min delay and typical preshock pressure of ~30 Torr, the maximum H_2O levels could not exceed a few parts per million. Computations performed in the present study for typical conditions in the shock experiments show that, for example, 2 ppm H_2O contaminant would have a negligible effect on experimental profiles. The amount required to have a significant effect on the results is much larger than for conditions used in the FGFAM study. The typically higher shock temperatures lead to larger R1 and R2 reaction rates with which the hypothetical hydrogenous species reactions must compete. These procedures to avoid H_2O contamination employed by the Davidson/Hanson group have been generally known in the shock tube community at least since the early 1970s. Though not frequently discussed in shock tube papers, it is suspected few, if any, of the other works have been seriously affected by this suggested factor. Therefore, the preponderance of evidence seems to indicate the results of ref 27 regarding k_2 are incorrect, and they are discarded. Perhaps the complications due to the increased importance of reactions −R7 and R8 at the higher pressures of that study are responsible for the discrepancy.

Further insight into selection among the studies may be obtained from an Arrhenius plot of k_{tot}, presented in Figure 6. In Figure 6, k_{tot} expressions are plotted. These were taken from sources in which both k_1 and k_2 or k_{tot} were measured, i.e., refs 6, 27, 60, 62c, 63, and 65. It should be noted that ref 60 contains individual expressions for k_1 and k_2. However, these were apparently obtained by making the assumption that $k_1 = k_2$. The author is not clear about this point. Only $[N_2O]$ was measured in that work. In the absence of other species profiles, such as NO and O_2, independent k_1 and k_2 data cannot be derived. A similar assumption, clearly stated, was used in ref 62. Thus, the main result pertinent to the present study from refs 60 and 62 is k_{tot}.

As can be seen in Figure 6, most of the k_{tot} expressions have similar slopes. However, they are divided into two groups whose absolute values are separated by approximately a factor of 2. The result of DDCH92 has a slightly smaller slope than the others, but covers a shorter temperature range than most. At the highest temperatures used in that study, the DDCH92 result agrees within error limits with either of the two sets of results shown. However, at the lowest temperatures used, the DDCH92 data clearly agree best with the higher k_{tot} set; thus, it belongs with that set. No clear reason could be found why the two sets of results differ from each other.

The choice of which set to use in fitting is influenced by the k_{-1} data from the four studies on NO mixtures previously selected as most reliable.[29,35−37] Data on k_{-1} from these studies were fitted, and the result was reversed to obtain a k_1 estimate. The expression obtained is also shown in Figure 6. If one assumes $k_1 = k_2$ at about 2000 K, i.e., $1/T = 5 \times 10^{-4}$ K^{-1}, then k_1 from the NO studies should be a factor of 2 below k_{tot} at this point. As can be seen in Figure 6, the k_1 from these studies is a factor of 2 below the higher set of k_{tot} results in Figure 6 at $1/T = 5 \times 10^{-4}$ K^{-1}. In addition, toward higher temperatures the k_1 expression lies below the higher set of k_{tot} values, but above the lower set. Obviously, concluding that k_1 is larger than k_{tot} cannot be logical (though the issue of error limits could make this feasible). Therefore, on the basis of comparison of k_{tot} values to the k_1 data from NO studies, the set having larger values in Figure 6, i.e., from DDCH92 and refs 60, 63, and 65, is selected. The temperature range to use with the expression of ref 60 was obtained by examination of data given in the

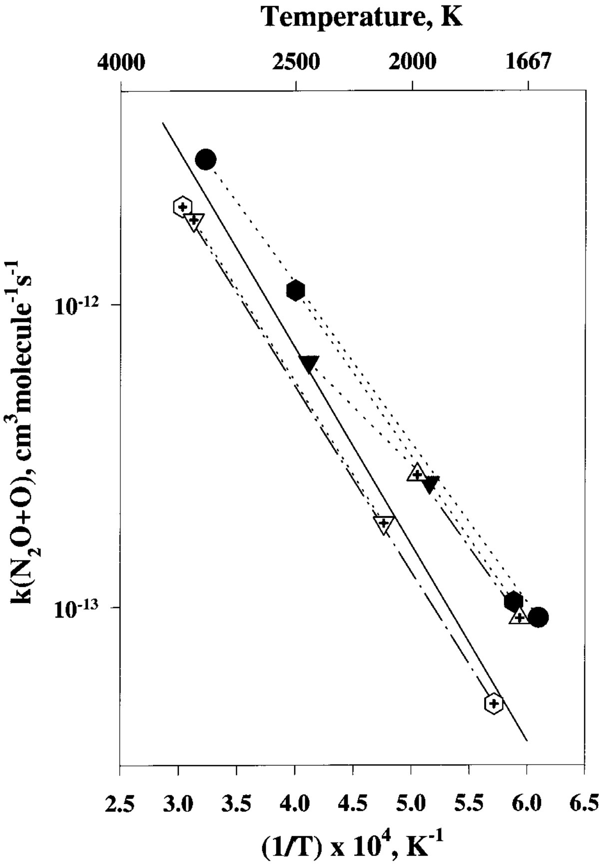

Figure 6. Arrhenius plots of k_{tot} results from several shock tube studies on N_2O/Ar mixtures. The k_1 expression obtained by fitting the four selected results from k_{-1} studies on NO mixtures and then reversing the resulting rate coefficient is also shown. Key: ⊕—·—⊕ Zuev and Starikovskii;[27] ▽·······▽ Dean, et al.;[62c] ●·······● Soloukhin;[60] ⬢·······⬢ Zaslonko, et al.;[63] ▼·······▼ DDCH92;[6] △—·—△ Sulzmann, et al.;[65] ——— k_1 from reversing the fit to k_{-1} values from the four best literature sources.

figures. The upper temperature limit for the k_1 expression from ref 63 is restricted to only 1910 K, rather than 2500 K claimed in the text; the plot[63] of the [NO] data on which it is based indicates only one point was taken above 1910 K. References 60 and 63 have previously gone largely unnoticed.

IV. Recommendations and Discussion

A synopsis of the data chosen for fitting by the reasoning of the earlier sections is given in Table 6. The expressions for k_{-1} from each of the four studies shown were first reversed to obtain k_1 values, and the individual results were then included in the fitted data set. The k_1, k_2, and k_{tot} expressions given were fitted to the equations

$$k_1 = A_1 \exp(-E_{a1}/RT) \qquad (1)$$

$$k_2 = A_2 \exp(-E_{a2}/RT) \qquad (2)$$

$$k_{tot} = k_1 + k_2 \qquad (3)$$

where A_i and E_{ai}, $i = 1, 2$, represent the Arrhenius A factors and activation energies, respectively. An attempt was made to fit the data to a six-parameter form, that is, including T^{ni} curvature factors in the k_1 and k_2 expressions. However, this approach yielded unrealistic results which will not be further discussed. All the data were fitted simultaneously using the multiparameter, nonlinear least-squares routine of Kotlar et al.[70] The fitted data were weighted according to error limits given in the studies (see Table 6). For the FGFAM data, the individual points were used. For the other sources, the given expressions were used. In order that each group's result is given proper weights for equal temperature intervals, points were calculated using the given expressions at intervals equal to the average spacing used in the FGFAM experiments. The fitted recommendations are

$$k_1 = 1.52 \times 10^{-10} \exp(-13930/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (1370-4080\ \mathrm{K}) \qquad (4)$$

$$k_2 = 6.13 \times 10^{-12} \exp(-8020/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (1075-3340\ \mathrm{K}) \qquad (5)$$

The fitted expressions are compared to the retained data in Figures 7−9. The comparison of the fitted expressions to the data is quite satisfactory. In Figure 8, note that k_1 data from studies on the reaction in both the reverse and forward directions agree very well. This is a strong indication that the assumption that the major products of the NO + NO reaction are O + N_2O is correct.

The temperature ranges for the recommended k_1 and k_2 expressions differ. This result is due to the fact that data which primarily affect one of the fitted expressions at the end of a

TABLE 6: Summary of Data Used for Obtaining Recommendations

source	data type	expression (cm^3 molecule^{-1} s^{-1})	error limit (%)	temp range (K)
		Data from NO Studies		
Kaufman et al.[29]	k_{-1}	$2.0 \times 10^{-12} \exp(-32110K/T)$	50[a]	1370−1530
McCullough et al.[35]	k_{-1}	$3.0 \times 10^{-12} \exp(-32110K/T)$	50[a]	1750−2100
Koshi and Asaba[36]	k_{-1}	$8.1 \times 10^{-12} \exp(-33770K/T)$	50[a]	2700−3500
Theilen and Roth[37]	k_{-1}	$1.5 \times 10^{-11} \exp(-35000K/T)$	40	2400−3450
		Data from N_2O studies		
Soloukhin[60]	k_{tot}	$1.5 \times 10^{-10} \exp(-12130\ K/T)$	50[a]	1640−3100
Zaslonko et al.[63]	k_1	$2.3 \times 10^{-10} \exp(-15100\ K/T)$	50	1680−1910
	k_{tot}	$1.7 \times 10^{-10} \exp(-12580\ K/T)$	50	1700−2500
Monat et al.[64]	k_1	$5.1 \times 10^{-11} \exp(-10970\ K/T)$	65	2380−4080
Sulzmann et al.[65]	k_1	$6.8 \times 10^{-11} \exp(-12350\ K/T)$	80	1685−2000
	k_{tot}	$1.4 \times 10^{-10} \exp(-12350\ K/T)$	75	1685−1980
DDCH92[6]	k_1	$4.8 \times 10^{-11} \exp(-11650\ K/T)$	15	1680−2430
	k_2	$2.3 \times 10^{-12} \exp(-5440\ K/T)$	25	1940−3340
FGFAM[1]	k_{tot}	see footnote b		1075−1140

[a] No error limit was given in the referenced work. Fifty percent, which is typical of experiments such as these, was assumed for the weighted fit. [b] Data fitted were the 10 measured points, with their individual error limits, at the lowest temperatures of the range studied in ref 1.

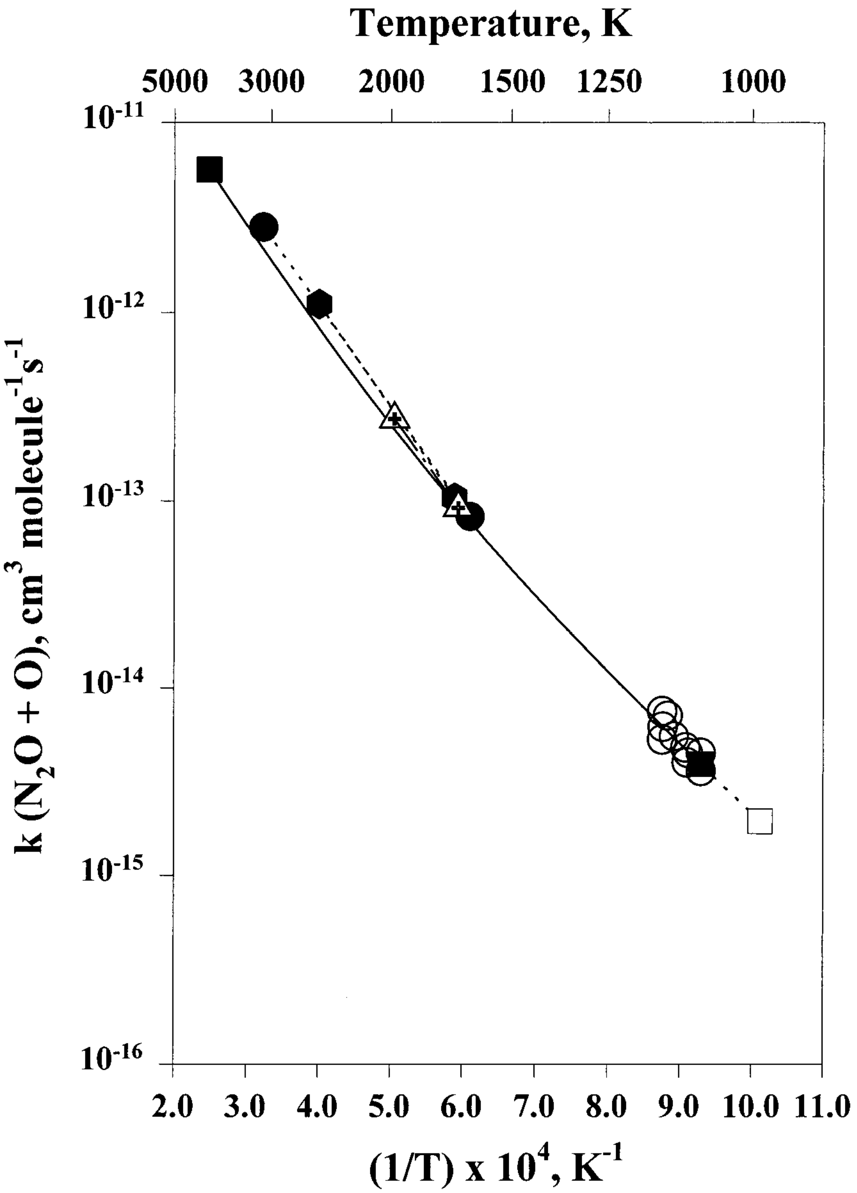

Figure 7. Arrhenius plot of selected results and recommendation for $k_{tot} = k_1 + k_2$. The portion of the line for the recommendation that is dashed with an open symbol represents extrapolation beyond the recommended temperature range. Key: ●·······● Soloukhin;[60] ⬢·······⬢ Zaslonko, et al.;[63] △— · —△ Sulzmann, et al.;[65] ○ FGFAM;[1] ■——■ recommendation for k_{tot} from the fit of retained data.

range do not necessarily strongly affect the other. For example, the fitted k_1 expression at the lower temperatures is largely determined by the Kaufman et al.[29] data on the reverse reaction, which end at 1370 K; the Kaufman et al. data do not strongly affect the fitted k_2, which is much larger at 1370 K. At the highest temperatures in the figures, k_1 is strongly affected by a number of data sets including the Monat et al.[64] result, which extends to 4080 K. The fitted k_2 expression is determined at the lowest temperatures primarily by the FGFAM results due to the fact that k_2 dominates the reaction at the temperatures of that study, 1075−1140 K (see below). The FGFAM results do not strongly affect the fitted k_1. The fitted k_2 at higher temperatures is determined primarily by the DDCH92 k_2 results, which had an upper limit of 3340 K. Error limits are assigned as a factor of 2 for the k_1 expression at 1370 K, decreasing to 1.5 at 1650 K, and remaining there throughout the rest of the range, and a factor of 1.5 for the k_2 expression over its entire range.

Preliminary ab initio calculations of Lin and co-workers[38] indicate the barrier to reaction R1 is about 28 kcal/mol. The E_a of the present recommended k_1 expression is 27.7 kcal/mol, which compares quite favorably to the ab initio barrier. The computed barrier for reaction R2 on the triplet reaction surface is much higher, indicating the reaction does not proceed on this surface. Lin and co-workers speculate that the reaction takes place via a crossing of the triplet and lowest singlet [i.e., $O(^1D) + N_2O$] surfaces and have started searching for the intersection point(s). We note the recommended k_2 expression has an *A* factor which seems somewhat small for a reaction which appears to be a simple atom abstraction. If Lin and co-workers are correct that reaction R2 takes place via surface crossing, this could explain the small *A* factor.

None of the earlier k_1 recommendations[2−5] differ strongly from the present result. HS85 is the most recent of these which involved selection of best data sets from the literature and fitting over those chosen. The present result is ~30% lower at 1000 K and ~15% higher at 4000 K than the HS85 result. The recommended k_2 expressions from the reviews all yield values very similar to k_1 over a wide temperature range, except for ref 5, which simply recommended the DDCH92 expressions. The

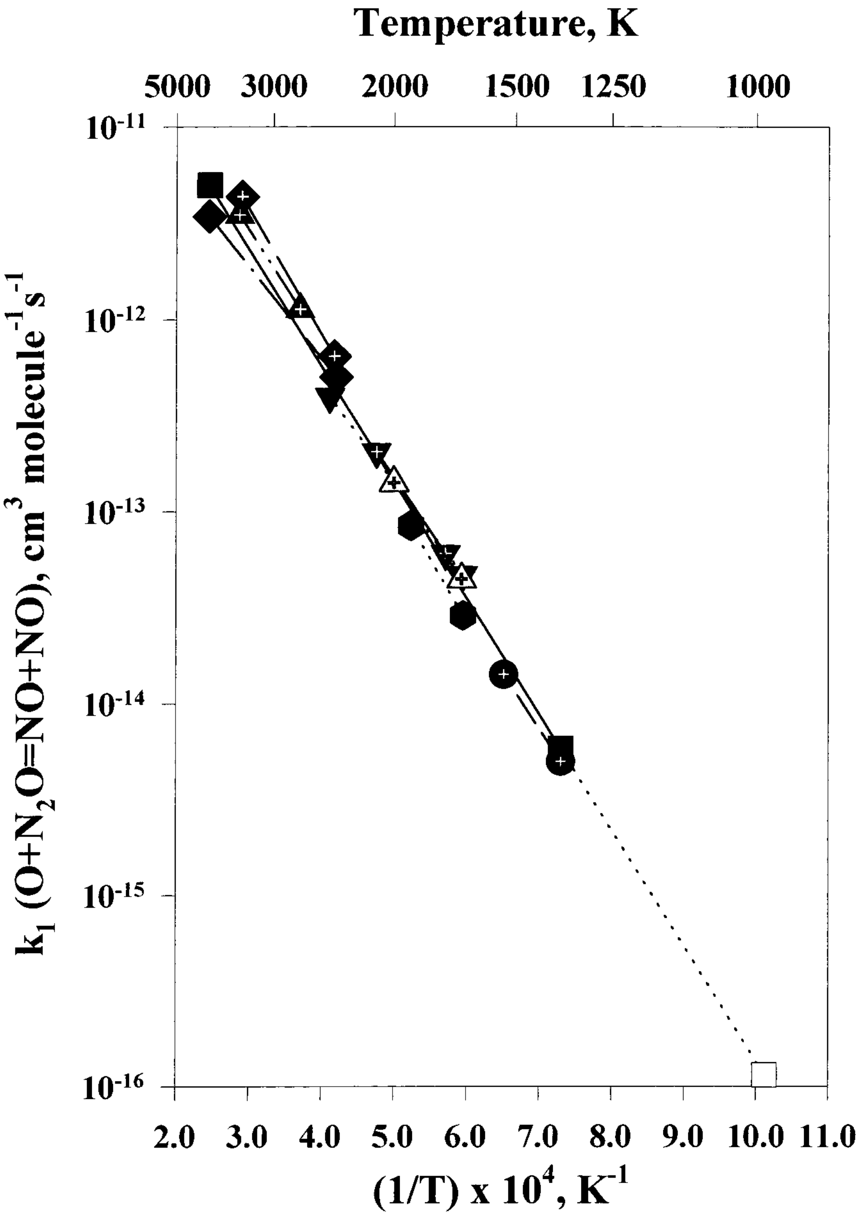

Figure 8. Arrhenius plot of selected results and recommendation for k_1. The solid symbols with white plus signs represent the rate expressions obtained from studies of the reverse reaction. The portion of the line for the recommendation for k_1 that is dashed with an open symbol represents extrapolation beyond the recommended temperature range. Key: ◆—·—◆ Monat, et al.;[64] ◆— —◆ Theilen and Roth;[37] ▲—··—▲ Koshi and Asaba;[36] ▼·······▼ DDCH92;[6] ▼——▼ McCullough, et al.;[35] △—·—△ Sulzmann et al.;[65] ⬢·······⬢ Zaslonko, et al.;[63] ●— — —● Kaufman, et al.;[29] ■——■ recommendation for k_1 from fit of retained data.

present k_1 and k_2 expressions are quite different from each other: k_2 is larger than k_1 at low temperatures and smaller at high temperatures. Extrapolation of the present recommendation for k_1 yields $k_2/k_1 = 9$ at 1100 K. Since k_{tot} at the temperatures of the FGFAM study is dominated by k_2, direct comparison to the DDCH92 study, as in Figure 9, is reasonable; the k_2 curve is only slightly below the k_{tot} curve at the FGFAM temperatures.

The recommended k_1 and k_2 expressions are equal at 1840 K. Thus, they fit the criterion mentioned earlier that most available data on the title reaction indicate the k_1 and k_2 expressions are equal at roughly 2000 K. The ratio k_1/k_2 is 0.67 at 1635 K and 1.5 at 2110 K. Thus, this ratio is fairly close to 1.0 over a wide temperature range in the region of shock tube studies. This fact, coupled with the possibly high estimate of temperatures in the mass spectrometer shock tube studies[58,59] and the results of ref 57, which are herein questioned, may be largely responsible for earlier recommendations that $k_1 = k_2$ over a much wider temperature range. The present results indicate that the earlier conclusion is erroneous.

V. Conclusion

An evaluation of the literature pertaining to the title reaction was performed, resulting in recommendations for its two major channels over wide temperature ranges. The evaluation process used detailed chemical modeling with recent information on important ancillary reactions and thermodynamics. There has been a wide spread in results concerning reactions R1, R2, and −R1. Serious mechanistic interpretation errors were newly identified in the present work in regard to several relevant studies, which have previously clouded the issue of the correct rate coefficient expressions. In particular, the assumption that

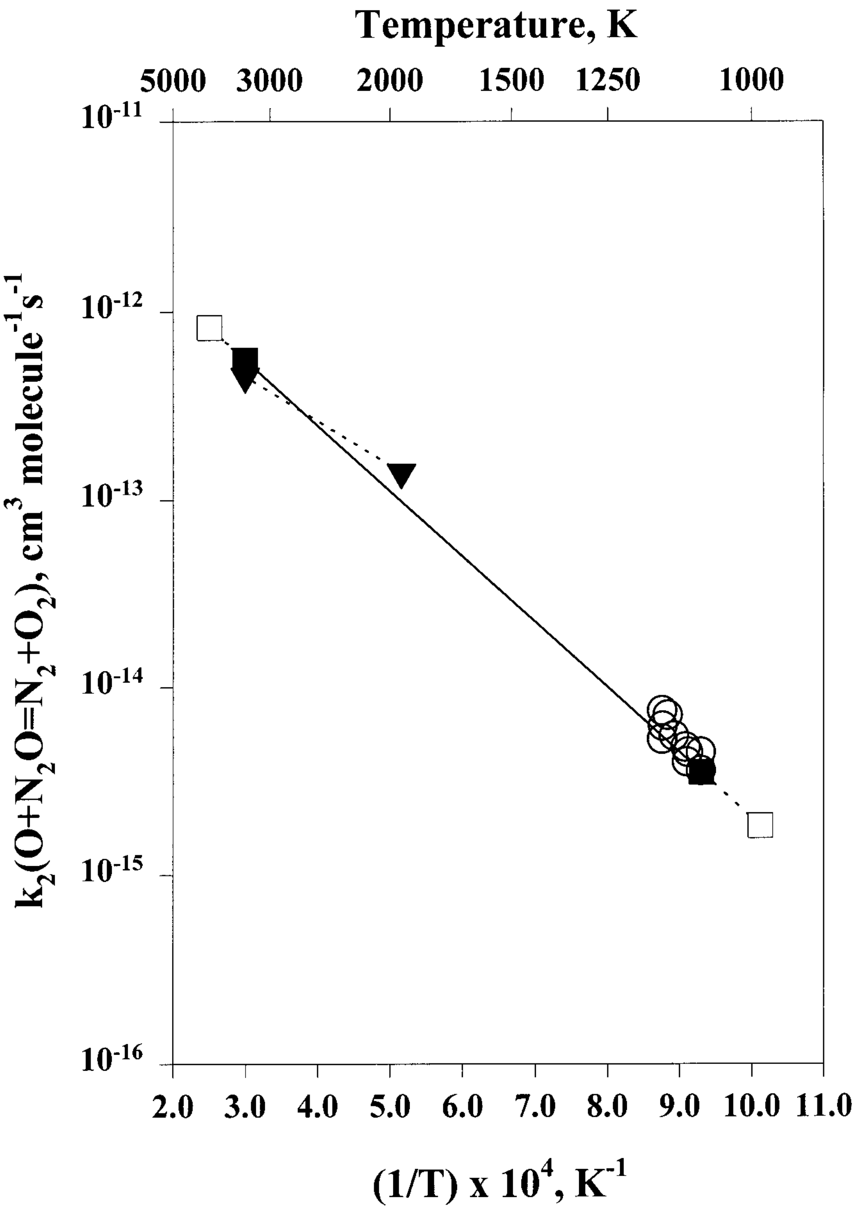

Figure 9. Arrhenius plot of selected results and recommendation for k_2. k_{tot} results from the FGFAM study[1] are also shown for comparison. At the temperature of the FGFAM study, k_2 accounts for approximately 90% of k_{tot}. The portions of the line for the recommendation for k_2 that are dashed with an open symbol represent extrapolation beyond the recommended temperature range. Key: ▼·······▼ DDCH92;[6] ○ FGFAM;[1] ■——■ recommendation for k_2 from the fit of retained data.

reaction R1 is the only source of NO in the burnt gases of the H$_2$/N$_2$O/O$_2$/H$_2$O flames studied by Fenimore and Jones[48] has been shown to be incorrect. This result is the central choice of the BDH73 recommendation, which affects most later recommendations. The results of Koshi and Asaba[36] regarding mechanistic errors in three other studies were confirmed. The present work demonstrates clear reasons why a number of results must be discarded. Results from the bulk of the remaining studies were fitted, and recommendations for k_1 and k_2 expressions were given. The most important point of these recommendations is that the O$_2$ + N$_2$ channel dominates the title reaction below ~1600 K and the NO + NO channel dominates above ~2100 K.

The study of Zuev and Starikovskii[27] served to focus our attention on possible effects of H$_2$O contamination on measurements relating to the title reaction. The modeling results yielded quantitative estimates of the amounts of H$_2$O necessary to strongly affect intermediate temperature results, such as reported in FGFAM, and also at higher temperature conditions typical of the shock tube experiments on N$_2$O/inert gas mixtures, as discussed herein. The results indicate H$_2$O contamination is unlikely to have caused significant problems for those studies. However, future workers should be aware of the potential difficulties this effect could pose in studying this chemical system.

Finally, it would be very helpful to have further ab initio calculations on this reaction. Only preliminary results[38] are currently available. In addition to calculations on reactions R1 and R2, estimates to confirm whether the only significant products of the NO + NO reaction are indeed O + N$_2$O, as seems likely and was assumed, are desirable.

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