Evaluated Chemical Kinetics Data for Reactions of $N(^2D)$, $N(^2P)$, and $N_2(A\,^3\Sigma_u^+)$ in the Gas Phase[a]

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Chemical kinetics data for the gas phase reactions of the first two electronically excited states of atomic nitrogen: $N(^2D)$ and $N(^2P)$, and of the first excited state of molecular nitrogen $N_2(A\,^3\Sigma_u^+)$ are compiled and evaluated. The experimental data for 127 reactions are summarized, the experimental method and year of publication given, a recommended value given for the rate constant for each reaction at 298 K, and where possible, its temperature dependence. The reaction mechanisms are discussed within the limits of the available quantitative product yield data. The literature has been covered through early 1999. There are 94 references. © *1999 American Institute of Physics and American Chemical Society.* [S0047-2689(99)00105-1]

Key words: air pollution, chemical kinetics, data evaluation, excited states, gas phase, nitrogen, plasma, rate coefficient.

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1. Introduction

The reactions of electronically excited species play an important role in plasma, laser, and atmospheric chemistry. The present review grew out of a need for reliable chemical kinetics rate data to be used in modeling the destruction of pollutants in air plasmas.[1] Although the focus of this review is on plasma chemistry, the scope has been expanded to include reactions which might not be relevant to that subject, but are of wider interest.

This review builds on the 1970 analysis of Donovan and Hussain on reactions of excited atomic species,[2] the 1979 evaluation of Schofield on excited state chemistry,[3] and the 1988 review of Golde[4] on reactions of $N_2(A\,^3\Sigma_u^+)$.

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2. Scope and Format

The purpose of this paper is to compile and evaluate data on reactions of the first two electronically excited states of atomic nitrogen: $N(^2D)$ and $N(^2P)$, and of the first excited state of molecular nitrogen $N_2(A\,^3\Sigma_u^+)$. Although every effort has been made to be complete, some earlier work has almost certainly been omitted, and certain classes of reaction such as the reactions of $N_2(A\,^3\Sigma_u^+)$ with the rare gases or with atomic species other than H, N, or O, are not included. Data are given for 129 reactions. Coverage is through early 1999.

The data are presented in two types of tables: summary tables which give recommended values, and data tables which compile the published data.

As an aid in assessing the reliability of the data, comparison tables are also provided which compare rate constants reported in selected publications. These tables cover a limited number of reactants and give the normalized rate constants at 298 K. They are discussed in more detail in the introductions to Secs. 4, 5, and 6. However, there is one common feature. Older values, often the results of pioneering studies, tend to be high. This reflects the fact that in subsequent work there is usually an improvement in sensitivity and overall technique.

The summary tables give the reaction, Arrhenius parameters if known, rate constant at or near 298 K, and an assigned uncertainty based on the breadth of studies or of the experimental method. The uncertainty is a factor to be used as a multiplier of the 298 K rate constant to provide the probable range of the recommended value.

Following the summary table, the reported experimental data are given for each reaction, either in a separate data table if there are extensive data, or in the text. Information on reaction mechanism, basis for the recommendation, and any other relevant information are included here. Where data are given in tabular form, the entries are arranged in chronological order of publication. These tables are not numbered.

The only exception to this format is Table 9, Recommended values for the rate constants of the reactions of $N_2(A\,^3\Sigma_u^+)$ with miscellaneous species, which is a compilation of data on a broad range of species, mostly the results of single measurements. For these data, the rate constants are tabulated at 298 K for $v=0$ and 1. If there are more than one measurement a recommended value may also be provided. If there are product data or information on other aspects of the reaction, it is discussed in a footnote to the table.

Throughout this review species in the ground electronic state are written without any designation, i.e., $N \equiv N(^4S)$; $N_2 \equiv N_2(X\,^1\Sigma_g^+)$.

All rate constants are bimolecular and given in units of $cm^3\,molecule^{-1}\,s^{-1}$.

The conversion factors used for energy terms are: $1\,kcal\,mol^{-1} = 4.184\,kJ\,mol^{-1}$; $1\,eV = 96.49\,kJ\,mol^{-1}$.

3. Experimental Methods and Their Reliability

As in all chemical kinetics measurements, the goal in studying excited state chemistry is to isolate the reaction of interest from all other competing or complicating processes. This is particularly difficult to achieve in the case of excited state reactions since the methods of production invariably involve formation of other reactive species, some of which may not even be identified. Ideally, the excited state reactant of interest would be produced by some form of pulsed irradiation and followed by optical absorption or fluorescence. Reactions of the excited states of atomic nitrogen have routinely been studied in this manner using, for example, flash photolysis or pulse radiolysis. However, even for this kind of experiment, great caution must be taken in interpreting the results since excited state species other than the desired one are also produced. Discharge-flow techniques have also been used in studying excited states of atomic nitrogen. The measurement of reaction time is more complex in these systems and potential complications arising from the presence of other active species are equally daunting. Note that the interfering species need not be excited. For example, ground state nitrogen atoms may react with $N_2(A\,^3\Sigma_u^+)$ to produce $N(^2P)$.

Pulse methods are most applicable to the excited atomic species; for the excited states of molecular nitrogen, with few exceptions, the only approach is to use the discharge flow technique. Some simplification can be had by exciting one of the rare gases such as argon, populating the first excited state, and then reacting this with N_2 to produce various excited states of N_2. This does not solve the problem of defining the states being studied, but at least simplifies the situation by eliminating problems arising from the formation of atomic species.

Experimental methods are discussed further at the start of each section.

It cannot be too strongly emphasized that the evaluation of the kinds of data covered in this review is highly subjective and fraught with uncertainty. The data resources are in many cases sparse, the experiments difficult, and the systems complex. In general, uncertainty factors of 1.3 are assigned to well studied reactions (two or more studies), while for single studies using established experimental methods, a factor of 2 is assigned to reflect the lack of confirmation. Limiting values are not assigned an uncertainty. Note that the author's reported error limits are not given, and all values are rounded to no more than two significant figures. No effort has been made to arrive at an error estimate based on a statistical analysis of the data, since in almost all reactions included here, the major sources of uncertainty are unknown systematic errors arising out of the complexity of the experimental systems. Additional sources of systematic error are in the measurement of time, particularly for flow systems, and in determination of the concentrations of the reactant or quencher species. In many cases experimental details as to sample preparation are not given.

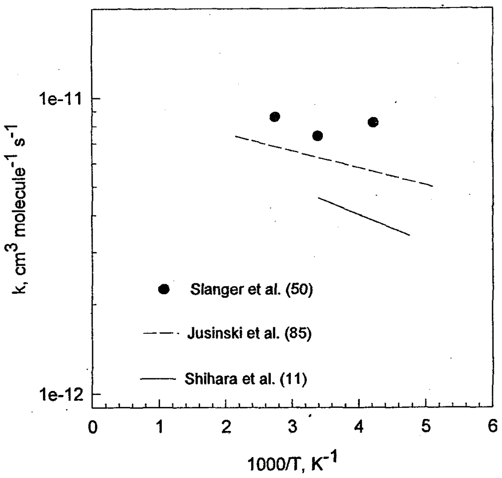

FIG. 1. Arrhenius plot for the reaction of N(^2D) with O_2.

No effort has been made to provide an error factor other than at 298 K. The data are not extensive enough to justify such a procedure. However, the uncertainty increases moving away from 298 K (see Figs. 1–3), and derived rate constants should be treated with caution at other temperatures.

In the data tables, the acronyms given below are used to indicate the experimental method. However, these are intended only to provide a rough classification of the methods, for details it is necessary to consult the original publication.

Methods of production:

(DF) discharge flow,
(FP) flash photolysis,
(LP) laser photolysis,
(P) steady state photolysis,
(PD) pulse discharge,
(PR) pulse radiolysis.

Methods of detection:

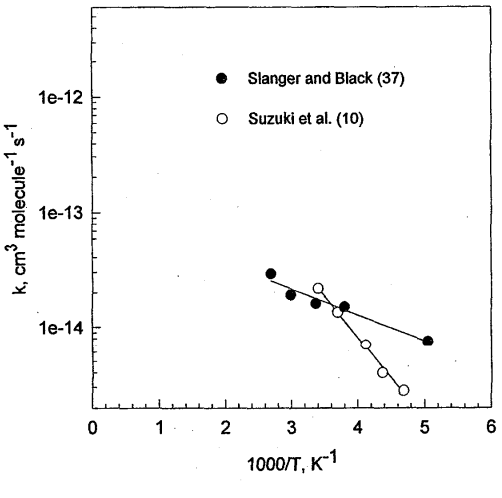

FIG. 2. Arrhenius plot for the reaction of N(^2D) with N_2.

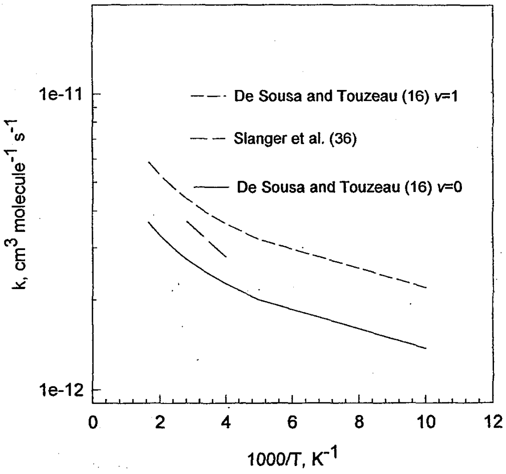

FIG. 3. Arrhenius plot for the reaction of $N_2(A\ ^3\Sigma_u^+)$ with O_2.

(CL) chemiluminescence (fluorescence),
(ES) emission spectroscopy,
(ESR) electron spin resonance,
(LIF) laser induced fluorescence,
(LPI) laser photoionization,
(REMPI) resonance enhanced multiphoton ionization,
(RA) resonance absorption,
(RF) resonance fluorescence.

4. Reactions of N(^2D)

Rate constants are given here for a total of 27 reactions of N(^2D). In general, there is reasonable agreement between different workers over a long period of time. Nonetheless, if we examine the data for a well studied reaction, for example, N(^2D)+H_2, for which there are nine sets of measurements, the range in rate constants is about a factor of 2. While one expects the measurement of rate constants for slow reactions to be difficult because of the limitations of measurement technique as well as the complications that might arise from the presence of reactive impurities (or products), for reactions of moderate reactivity one expects the measurements to be more routine. The spread in values indicates that there are sources of systematic error in many of these systems that have not been recognized.

The internal consistency of measurements from a single study can be examined by comparing the normalized rate constants for the most widely studied reactions. This is shown in Table 1. Although only qualitative conclusions can be drawn, the values in Table 1 suggest that the data of Black *et al.*,[7] of Fell *et al.*,[43] and the earlier results of Husain *et al.*,[52] are too high. Recognizing that there are glaring exceptions to that statement, e.g., Black *et al.*[7] have a low value for the methane reaction, we choose to disregard these data in arriving at recommended values if there are other data available. We note that the earlier work of Black *et al.*[7] is followed in later publications (Black *et al.*,[72] Slanger and Black)[37] with results in better agreement with the average

TABLE 1. Rate constants normalized to the average value of the rate constant for the reactions of $N(^2D)$ with selected reactants

Source	Year	H_2	O_2	NO	N_2O	N_2	CH_4	C_2H_4	CO	CO_2
Black *et al.*[7]	1969	1.89	1.11	2.21	1.13		0.74	1.50	1.84	1.30
Lin and Kaufman[44]	1971		0.95	0.86	1.31	0.88				1.08
Slanger *et al.*[50]	1971		1.29		0.60					
Husain *et al.*[52]	1972	0.64	1.48	0.75	1.80	1.27				
Husain *et al.*[14]	1974	0.79	0.83	0.73	0.60	0.83			0.64	0.39
Black *et al.*[72]	1975	1.02			0.98					
Slanger and Black[37]	1976				0.64	0.99				
Iannuzzi and Kaufman[39]	1980		0.86							
Sugawara *et al.*[67]	1980			0.43		0.72		0.46		
Fell *et al.*[43]	1981	1.32	0.97		1.13		1.13	1.04		1.47
Piper *et al.*[49]	1987	0.87	0.73		0.83				0.52	0.76
Whitefield and Hovis[42]	1987	0.68	1.05							
Jusinski *et al.*[85]	1988		1.00							
Suzuki *et al.*[10]	1993	0.91				1.32				
Shihira *et al.*[11]	1994		0.75							
Umemoto *et al.*[92]	1998	0.86		1.02			0.81			
Takayanagi *et al.*[90]	1999						1.33			

values. Similarly, the earlier results of Husain *et al.*[52] are followed by lower values in later work (Husain *et al.*[14]).

Husain and his co-workers (see Ref. 14) used pulsed vacuum ultraviolet flash lamps to photolyze N_2O to produce both $N(^2D)$ and $N(^2P)$. The excited state concentrations were monitored by absorption of resonance radiation from a flowing nitrogen cw discharge lamp. This in principle should be a very accurate measurement method. The limitations have to do with impurities and the measurement of reactant (quencher) concentration. The body of data obtained by this method is extensive[14] and, with few exceptions, should be reliable.

Young (and later Slanger) and their co-workers (see Ref. 7) also used pulsed vacuum ultraviolet flash lamps to photolysis N_2O to produce both $N(^2D)$ and $N(^2P)$. They monitored the excited state reactions by measuring the attenuation of $NO(B\,^2\Pi)$ emission arising from the reaction $N(^2D)+N_2O\rightarrow N_2+NO(B\,^2\Pi)$ or emission arising from the $N(^2P)-N(^4S)$ transition. Although the earlier reported numbers (Black *et al.*[7]) appear to be high, the later values are in better agreement with the consensus values.

The discharge flow method was used by Kaufman and his co-workers (see Ref. 44). In this method, the excited atoms are produced by a discharge in He or Ar containing a small amount of N_2, and monitored by absorption of resonance radiation from a He or Ar–N_2 flowing cw discharge lamp. In these experiments, time is measured as flow velocity. These measurements also led to a consistent and reliable body of data.

Most subsequent measurements are based on the flash photolysis or discharge flow methods. Thus, Fell *et al.*[43] used a flow system with electron spin resonance detection rather than resonance absorption to monitor $N(^2D)$. They measured rate constants for a large number of reactants, particularly hydrocarbons. In general, their results are uniformly higher than those of other workers, and when theirs is the only data, their values have been adjusted downward by a factor of 0.6 to arrive at the recommended value.

Rate constants measured using the pulse radiolysis–resonance absorption technique (PR–RA)[10,11,67,81,90,92] which are taken near 10^5 Pa, are compatible with those obtained at much lower pressures (there is no indication of a pressure effect, but see Sec. 5). This approach, which involves producing the excited states by pulse radiolysis and monitoring the concentrations by resonance absorption, would appear to provide a reliable method; the reaction can be followed over a long time period and the concentrations of reactants varied widely. It is unfortunate that where there are data to compare (nitrogen and methane) they disagree by about factors of 2.

Umemoto *et al.*[92] have used a pulsed laser photolysis method to produce the excited states from NO, which were then followed by laser pumping the excited states into upper states from which they fluoresced. In principal this should provide a very powerful measurement method. As can be seen from Table 1 there are as yet unresolved differences between theirs and other workers data. Some of these are discussed further under the individual reactions. Recommended values for the rate constants of the reactions of $N(^2D)$ are given in Tables 2 and 3.

Most of the reactions of $N(^2D)$ discussed here have available exothermic adiabatic reaction paths and are fast, but generally, product data are not available. Fell *et al.*[43] in their study of the reactions of hydrocarbons observed CN emission bands in these systems, although their origin is unclear. One possible source is from the reaction $N_2(A\,^3\Sigma_u^+)+CN\rightarrow N_2+CN(B^2_{\Pi})$.[74] Furthermore, it is known that hydrocarbons are unreactive towards $N(^4S)$, whereas hydrocarbon radicals are very reactive. Any highly reactive species could initiate reaction which would then be carried by radical chain reactions. The recent *ab initio* studies of the reactions of $N(^2D)$ with methane[47] and ethylene[93] are providing the first real information on the mechanisms of the hydrocarbon reactions.

TABLE 2. Recommended values for the rate constants of the reactions of N(^2D) with species containing H, O, F, N, and S[a]

Reaction	A	E/R	$k(298)$	$f(298)$[b]	Notes
$N(^2D)+H_2=NH+H$	4.2×10^{-11}	880	2.2×10^{-12}	1.3	200–300 K
$N(^2D)+H_2O=$products			4×10^{-11}	2	
$N(^2D)+NH_3=$products			5×10^{-11}	2	
$N(^2D)+HF=$products			1×10^{-12}	2	
$N(^2D)+O=N+O(^3P,^1D)$	3.3×10^{-12}	260	1.4×10^{-12}	2	300–400 K
$N(^2D)+O_2=NO+O(^3P,^1D)$	9.7×10^{-12}	185	5.2×10^{-12}	1.3	200–500 K
$N(^2D)+NO=N_2+O(^3P,^1D,^1S)$			6×10^{-11}	1.5	
$N(^2D)+N_2O=N_2+NO$	1.5×10^{-11}	570	2.2×10^{-12}	1.3	200–400 K
$N(^2D)+N_2=N+N_2$			1.7×10^{-14}	1.5	
$N(^2D)+NF(a)=N_2(b)+F$			2.5×10^{-10}	2	
$N(^2D)+NF_3=N+NF_3$			3.0×10^{-13}	2	
$N(^2D)+SF_6=$products			$\leqslant10^{-14}$		

[a] Preexponential factors, A, and rate constants, $k(298)$, in units of $cm^3\,molecule^{-1}\,s^{-1}$; E/R in units of K.
[b] Multiplicative error factor. Applies to 298 K values only. Error limits are larger at lower or higher temperatures.

$N(^2D)+H_2\rightarrow NH+H$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Black *et al.*[7]	1969	FP–CL	5×10^{-12}
Husain *et al.*[52]	1972	FP–RA	1.7×10^{-12}
Husain *et al.*[14]	1974	FP–RS	2.1×10^{-12}
Black *et al.*[72]	1975	FP–CL	2.7×10^{-12}
Fell *et al.*[43]	1981	DF–ESR	3.5×10^{-12}
Piper *et al.*[49]	1987	DF–RF	2.3×10^{-12}
Whitefield and Hovis[42]	1987	DF–RA	1.8×10^{-12}
Suzuki *et al.*[10]	1993	PR–RA	2.4×10^{-12}
Umemoto *et al.*[92]	1998	LP–LIF	2.3×10^{-12}

Suzuki *et al.*[10] have studied the reaction over the temperature range 213–300 K, and reported $k=4.6\times10^{-11}\times\exp(-880/T)\ cm^3\,molecule^{-1}\,s^{-1}$. The same authors also reported for the reaction with D_2, $k=3.9\times10^{-11}\times\exp(-970/T)\ cm^3\,molecule^{-1}\,s^{-1}$. Umemoto *et al.*[92] also reported for D_2, $k=1.4\times10^{-12}\ cm^3\,molecule^{-1}\,s^{-1}$, and for HD, $k=1.8\times10^{-12}\ cm^3\,molecule^{-1}\,s^{-1}$.

In general the data are in good agreement. The recommended room temperature rate constant, $k=2.2\times10^{-12}\ cm^3\,molecule^{-1}\,s^{-1}$, is an average of all values excluding the data of Black *et al.*[7] and Husain *et al.*[52] The data of Fell *et al.*[43] were adjusted downwards by a factor of 0.6. The room temperature value was then used in conjunction with the temperature coefficients reported by Suzuki *et al.*[10] to derive the rate expression given in Table 2.

Although $NH(X\,^3\Sigma^-)$ has been observed as a product by several workers,[30,68] and may be produced in unit yield, there are no quantitative data. Scattering and trajectory calculations have been reported by Takayanagi *et al.*[35] and Kobayashi *et al.*[69] Both groups reported rate constants in reasonable agreement with experiment. The question of abstraction versus insertion has been the subject of controversy. On the basis of the measured vibrational distribution of the NH product ($v=1-3$) and a derived value for $v=0$, Dodd *et al.*[68] inferred that the reaction was abstraction. The nascent vibrational population ratios $NH(v=1)/NH(v=0)$ were measured by Umemoto and Matsumoto[30] to be 0.9, which led them to conclude that the absence of a strongly inverted vibrational distribution argues against a simple abstraction mechanism. See also the discussion for $N(^2D)+CH_4\rightarrow$products. For a discussion of the reaction paths for the $N(^2D)+H_2$ and $N(^2P)+H_2$ reactions see Donovan and Husain[2] and the further discussion by Schofield.[3]

$N(^2D)+H_2O\rightarrow NH+OH$
$N(^2D)+H_2O\rightarrow H+HNO$
$N(^2D)+H_2O\rightarrow H_2+NO$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Slanger and Black[37]	1976	FP–CL	2.5×10^{-10}
Umemoto *et al.*[92]	1998	LP–LIF	4.2×10^{-11}

The LP–LIF technique is more sensitive than the FP–CL technique and thus the recommended value is based on the data of Umemoto *et al.*[92] However, measurement of the partial pressure of water is not straightforward, and this is reflected in the assigned uncertainty.

Kurosaki and Takayanagi[91] have carried out an *ab initio* study of the reaction, and concluded that the main product channels were NH+OH, H+HNO, and H_2+NO. A nonadiabatic process may be important for the H_2+NO channel. The products can all be formed by insertion followed by decomposition of the initially formed HNOH intermediate. However, this does not rule out a possible direct abstraction channel. The authors also reported unpublished experimental data supporting the product identification [H. Umemoto, T. Asai, H. Hashimoto, and T. Nakae, J. Phys. Chem. A (in press)]. However, there are no quantitative product yield data.

$N(^2D)+NH_3 \rightarrow$ products

The only measurement is by Black *et al.*,[7] using the flash photolysis–chemiluminescence technique, who reported $k = 1.1\times10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$. Schofield[3] recommends $k \cong 5\times10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$, and that value is retained. There are no product data. NH and NH_2 are possible products.

$N(^2D)+HF \rightarrow$ products

The only measurement is by Whitefield and Hovis,[42] using the discharge flow–resonance absorption technique, who reported $k = 1\times10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$. There are no product data. Aside from physical quenching, the possible products include NH and NF both of which can be formed in the ground state in an exothermic reaction.

$N(^2D)+O \rightarrow O(^3P,^1D)+N$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Davenport *et al.*[83]	1976	DF–RF	1.8×10^{-12} (315 K)
Iannuzzi and Kaufman[39]	1980	DF–RF	1.8×10^{-12}
Jusinski *et al.*[85]	1988	DF–REMPI	21×10^{-12}
Piper[40]	1989	DF–RA	1.1×10^{-12}

Jusinski *et al.*[85] studied the reaction from 196 to 465 K, and reported $k = 3.4\times10^{-11}\exp(-145/T)\,cm^3\,molecule^{-1}\,s^{-1}$. The data of Davenport *et al.*[83] are relative to the rate constant for the reaction with O_2, for which they used $k = 5.5\times10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$. These workers also compared the rate constant ratios over the temperature range 315–400 K, and proposed the rate expression $k = 4\times10^{-12}\exp(-259/T)\,cm^3\,molecule^{-1}\,s^{-1}$. These workers used a somewhat different set of temperature coefficients for the comparison reaction than recommended here, but the differences are small, and no effort has been made to modify their derived temperature dependence for the $N(^2D)+O$ reaction.

The data of Jusinski *et al.*[85] are in serious disagreement with the results of the other three studies, one of which (Davenport *et al.*[83]), is from the same laboratory as Jusinski *et al.*[85] Piper[40] has discussed the data reported by Jusinski *et al.*,[85] and argued that their experiments were subject to large systematic errors.

The recommended value is based on the temperature dependence reported by Davenport *et al.*[83] adjusted to a 298 K value of $k = 1.4\times10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$, which is an average of the data of Iannuzzi and Kaufman[39] and of Piper.[40]

The most probable oxygen atom product is $O(^3P)$, but it is not possible to rule out some contribution by $O(^1D)$ (see Ref. 40).

$N(^2D)+O_2 \rightarrow O(^3P,^1D)+NO$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Black *et al.*[7]	1969	FP–CL	7×10^{-12}
Lin and Kaufman[44]	1971	DF–RA	6×10^{-12}
Husain *et al.*[52]	1972	FP–RA	9.3×10^{-12}
Slanger *et al.*[50]	1971	FP–CL	8.1×10^{-12}
Husain *et al.*[14]	1974	FP–RA	5.2×10^{-12}
Iannuzzi and Kaufman[39]	1980	DF–RF	5.4×10^{-12}
Fell *et al.*[43]	1981	DF–ESR	6.1×10^{-12}
Piper *et al.*[49]	1987	DF–RF	4.6×10^{-12}
Whitefield and Hovis[42]	1987	DF–RA	6.6×10^{-12}
Jusinski *et al.*[85]	1988	DF–REMPI	6.3×10^{-12}
Shihira *et al.*[11]	1994	PR–RA	4.7×10^{-12}

The earlier value of Lin and Kaufman[44] has been superseded by the data reported by Iannuzzi and Kaufman.[39] Both the earlier results of Black *et al.*[7] and Slanger *et al.*[50] and those of Husain *et al.*[52] are high and are discounted. The recommended room temperature rate constant, $k = 5.2\times10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$, is an average of the remaining reported data in which the value of Fell *et al.*[43] was adjusted downwards by a factor of 0.6 (see the introduction to this section).

Slanger *et al.*[50] measured rate constants at three temperatures: $k(231\,K) = 8.2\times10^{-12}$, $k(295\,K) = 7.4\times10^{-12}$, and $k(365\,K) = 8.6\times10^{-12}$, all in units of $cm^3\,molecule^{-1}\,s^{-1}$. They fitted these data to a $T^{1/2}$ temperature dependence. However, it is difficult to see any real temperature dependence in their data (see Fig. 1). The average is given above. Jusinski *et al.*[85] studied the reaction over the temperature range 196–465 K, and reported $k = 9.9\times10^{-12}\exp(-133/T)\,cm^3\,molecule^{-1}\,s^{-1}$. Their data are badly scattered. Shihira *et al.*[11] also measured the rate constant as a function of temperature over the range 210–295 K, and reported $k = 9.4\times10^{-12}\exp(-210/T)\,cm^3\,molecule^{-1}\,s^{-1}$. The various temperature dependent data are shown in Fig. 1. The most extensive data sets are from Jusinski *et al.*[85] and Shihira *et al.*[11] The agreement between these is very good above 300 K, becoming poorer moving below 300 K. The rate coefficients recommended in Table 2 are based on the recommended room temperature rate constant and an Arrhenius preexponential factor $A = 9.7\times10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$ (based on the data of Refs. 11 and 85), which leads to the expression $k = 9.7\times10^{-12}\exp(-185/T)\,cm^3\,molecule^{-1}\,s^{-1}$.

Lin and Kaufman[44] measured the O atom yield from the reaction and found 2.4 for each $N(^2D)$ reacted, close to the theoretical limit of 2.0, based on the probable mechanism: $N(^2D)+O_2 \rightarrow O+NO$, followed by $N+NO \rightarrow N_2+O$. This suggests that the reaction leads stoichiometrically to O atoms. The branching ratio for the channel leading to $O(^1D)$ has been reported to be 0.76 at 100 K.[46]

$N(^2D)+NO \rightarrow N_2+O(^3P,^1D,^1S)$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Black *et al.*[7]	1969	FP–CL	1.8×10^{-10}
Lin and Kaufman[44]	1971	DF–RA	7×10^{-11}
Husain *et al.*[52]	1972	FP–RA	6.1×10^{-11}
Husain *et al.*[14]	1974	FP–RA	5.9×10^{-11}
Sugawara *et al.*[67]	1980	PR–RA	3.5×10^{-11}
Umemoto *et al.*[92]	1998	LP–LIF	8.3×10^{-11}

The earlier results of Black *et al.*[7] and of Husain *et al.*[52] are discounted. The low value reported by Sugawara *et al.*[67] has been attributed to a flaw in their method of obtaining the NO partial pressure.[92] [See also the section on the $N(^2D)+N_2$ reaction.]

The recommended room temperature rate constant, $k=6\times10^{-11}$ cm^3 molecule^{-1} s^{-1} is based on the data of Lin and Kaufman,[44] Husain *et al.*,[14] and Umemoto *et al.*[92]

Although there are no product data, the reaction almost certainly leads to N_2+O.[2]

$N(^2D)+N_2O \rightarrow N_2+NO$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Black *et al.*[7]	1969	FP–CL	3×10^{-12}
Slanger *et al.*[50]	1971	FP–CL	1.6×10^{-12}
Lin and Kaufman[44]	1971	DF–RA	3.5×10^{-12}
Husain *et al.*[52]	1972	FP–RA	4.8×10^{-12}
Herbelin and Cohen[9]	1973	DF–CL	$\approx7\times10^{-13}$
Husain *et al.*[14]	1974	FP–RA	1.6×10^{-12}
Black *et al.*[72]	1975	FP–CL	2.6×10^{-12}
Slanger and Black[37]	1976	FP–CL	1.7×10^{-12}
Fell *et al.*[43]	1981	DF–ESR	3.0×10^{-12}
Piper *et al.*[49]	1987	DF–RF	2.2×10^{-12}

The earlier results of Black *et al.*,[7] Slanger *et al.*,[50] and those of Husain *et al.*[52] are high and are discounted. The recommended room temperature rate constant, $k=2.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, is an average of the remaining reported data (excluding limiting values) in which the value of Fell *et al.*[43] was adjusted downwards by a factor of 0.6 (see the Introduction to this section).

There have been two studies of the temperature dependence from the same laboratory (Slanger *et al.*[50] and Slanger and Black[37]). The data are in agreement. The data of Slanger and Black[37] cover a wider temperature range and yield the Arrhenius expression $k=1.15\times10^{-11}\exp(-570/T)$ cm^3 molecule^{-1} s^{-1}. The rate coefficients given in Table 2 are based on the recommended room temperature rate constant and the temperature dependence reported by Slanger and Black.[37]

Lin and Kaufman[44] measured the O atom yield to be 1.3 for each $N(^2D)$ reacted, close to the theoretical limit of 1.0, based on the probable mechanism: $N(^2D)+N_2O\rightarrow N_2+NO$, followed by $N+NO\rightarrow N_2+O$. This suggests that the reaction leads stoichiometrically to NO.

$N(^2D)+N_2 \rightarrow N+N_2$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Black *et al.*[7]	1969	FP–CL	$\leq6\times10^{-15}$
Lin and Kaufman[44]	1971	DF–RA	1.6×10^{-14}
Husain *et al.*[52]	1972	FP–RA	2.3×10^{-14}
Husain *et al.*[14]	1974	FP–RA	1.5×10^{-14}
Black *et al.*[72]	1975	FP–CL	$\leq1.8\times10^{-14}$
Slanger and Black[37]	1976	FP–CL	1.8×10^{-14}
Sugawara *et al.*[67]	1980	PR–RA	1.3×10^{-14}
Suzuki *et al.*[10]	1993	PR–RA	2.4×10^{-14}

The earlier results of Black *et al.*[7] and of Husain *et al.*[52] are discounted. The recommended room temperature rate constant, $k=1.7\times10^{-14}$ cm^3 molecule^{-1} s^{-1}, is an average of the data reported in Refs. 44, 14, 37, 67, and 10. The disagreement between the results of Sugawara *et al.*[67] and of Suzuki *et al.*[10] is hard to understand since the work was done in the same laboratory using the same technique. There is no basis for choosing between the two.

Slanger and Black[37] studied the reaction over the temperature range 198–372 K, and reported $k=1.0\times10^{-13}\times\exp(-510/T)$ cm^3 molecule^{-1} s^{-1}. Suzuki *et al.*[10] studied the reaction from 213 to 294 K, and give $k=5.4\times10^{-12}\times\exp(-1620/T)$ cm^3 molecule^{-1} s^{-1}. The data are in reasonable agreement at room temperature, but deviate sharply at lower or higher temperatures, as shown in Fig. 2. The disagreement on temperature coefficients is so great that no recommendation is provided.

The low reactivity is a consequence of the lack of an available adiabatic path.[2] Physical quenching to $N(^4S)$ is probably the only process.

$N(^2D)+NF(a\,^1\Delta) \rightarrow N_2(B\,^3\Pi_g)+F$

Davis and Piper[71] using the discharge flow–resonance absorption technique reported $k=2.5\times10^{-10}$ cm^3 molecule^{-1} s^{-1}. These workers monitored $N(^2D)$, $NF(a\,^1\Delta)$, and $N_2(B\,^3\Pi_g)$ to confirm the mechanism.

$N(^2D)+NF_3 \rightarrow$ products

Davis and Piper[71] reported $k=3.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, derived from unpublished data from their laboratory. The method was not specified, but probably involved discharge flow–resonance absorption. There are no product data.

TABLE 3. Recommended values for the rate constants of the reactions of $N(^2D)$ with species containing C[a]

Reaction	A	E/R	$k(298)$	$f(298)$[b]	Notes
$N(^2D)+CH_4 \rightarrow$ products	4.8×10^{-12}	750	4.0×10^{-12}	1.5	
$N(^2D)+CH_3F \rightarrow$ products			1.0×10^{-12}	2	
$N(^2D)+CF_3H \rightarrow$ products			1.0×10^{-13}	2	
$N(^2D)+CF_4 \rightarrow$ products			$\leq10^{-14}$		
$N(^2D)+C_2H_6 \rightarrow$ products			1.9×10^{-11}	1.5	
$N(^2D)+C_2F_6 \rightarrow$ products			$\leq10^{-14}$		
$N(^2D)+C_3H_8 \rightarrow$ products			2.9×10^{-11}	1.5	
$N(^2D)+n\text{-}C_4H_{10} \rightarrow$ products			3.1×10^{-11}	2	
$N(^2D)+\text{neo-}C_5H_{12} \rightarrow$ products			2.8×10^{-11}	2	
$N(^2D)+C_2H_4 \rightarrow$ products			4.3×10^{-11}	1.5	
$N(^2D)+CH_2CF_2 \rightarrow$ products			3.2×10^{-11}	2	
$N(^2D)+C_3H_6 \rightarrow$ products			6.6×10^{-11}	2	
$N(^2D)+C_2H_2 \rightarrow$ products	1.6×10^{-10}	270	6.5×10^{-11}	1.3	220–300 K
$N(^2D)+CO \rightarrow$ products			1.9×10^{-12}	1.3	
$N(^2D)+CO_2 \rightarrow NO+CO$			3.6×10^{-13}	1.5	

[a] Preexponential factors, A, and rate constants, $k(298)$, in units of $\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$; E/R in units of K.

[b] Multiplicative error factor. Applies to 298 K values only. Error limits are larger at lower or higher temperatures.

$N(^2D)+SF_6 \rightarrow$ products

Fell *et al.*,[43] using the discharge flow–electron spin resonance technique, reported a limiting value for the rate constant of $k \leq 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$. There are no exothermic product channels.

$N(^2D)+CH_4 \rightarrow H+CH_2NH$
$N(^2D)+CH_4 \rightarrow NH+CH_3$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Black *et al.*[7]	1969	FP-CL	3×10^{-12}
Fell *et al.*[43]	1981	DF-ESR	4.6×10^{-12}
Umemoto *et al.*[92]	1998	LP-LIF	3.3×10^{-12}
Takayanagi *et al.*[90]	1999	PR-RA	5.4×10^{-12} (292 K)

Takayanagi *et al.*[90] studied the reaction over the temperature range 223–292 K, and reported $k=7.1\times10^{-11} \times\exp(-750/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$.

There are also data for the deuterated analogues. Umemoto *et al.*[92] give $k(CH_3D)=3.2\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$, $k(CH_2D_2)=2.7\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$, $k(CHD_3)=2.3\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$, and $k(CD_4)=2.0\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$. Takayanagi *et al.*[90] reported $k(CD_4)=3.3\times10^{-11}\exp(-700/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ [the rate constant at 298 K is $k(CD_4)=3.2\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$, considerably greater than that reported by Umemoto *et al.*[92]].

The recommended value at 298 K is an average of the values reported by Fell *et al.*[43] (adjusted downwards by a factor of 0.6), Umemoto *et al.*,[92] and Takayanagi *et al.*[90] The recommended temperature coefficients are based on the recommended value at 298 K and the temperature dependence of Takayanagi *et al.*[90]

Umemoto *et al.*[84] have studied the nascent rotational and vibrational distributions for the product $NH(X\,^3\Sigma^-)$. They concluded that the reaction involves insertion rather than abstraction, having many similarities to the well characterized insertion reactions of $O(^1D)$ with alkanes. Kurosaki *et al.*,[47] carried out *ab initio* calculations which also indicated that the reaction is insertion followed by decomposition via several channels. These workers also carried out Rice–Ramsperger–Kassel–Marcus (RRKM) calculations to derive thermal rate constants, but their method is not quantitative. They estimate that the barrier for insertion is less that $4\ \text{kJ}\ \text{mol}^{-1}$. Assuming an insertion reaction, they concluded that the major decomposition channels of the initially formed intermediate was to CH_3+NH and CH_2NH+H. More recently, Umemoto *et al.*,[94] reported the yields of NH and H to be 0.3 and 0.8, respectively, confirming the insertion mechanism.

$N(^2D)+CH_3F \rightarrow$ products

The only measurement is by Fell *et al.*,[43] using the discharge flow–electron spin resonance technique. They reported $k=1.6\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$; this has been adjusted downwards by a factor of 0.6 to obtain the recommended value (see the discussion in the introduction to this section). There are no product data. The reaction is probably insertion. CH_2F+NH may be formed in an exothermic reaction.

$N(^2D)+CF_3H \rightarrow$ products

The only measurement is by Fell *et al.*,[43] using the discharge flow–electron spin resonance technique. They reported $k=1.6\times10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$; this has been adjusted downwards by a factor of 0.6 to obtain the recommended value (see the discussion in the introduction to this section). The reaction is probably insertion leading to CF_3+NH, which is an exothermic path. However, there are no product data.

$N(^2D)+CF_4 \rightarrow$ products

Fell *et al.*,[43] using the discharge flow–electron spin resonance technique, reported a limiting value for the rate constant of $k \leqslant 10^{-14}$ cm^3 molecule^{-1} s^{-1}. There are no product data. The reaction is probably all physical quenching; there are no exothermic product channels.

$N(^2D)+C_2H_6 \rightarrow$ products

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Fell *et al.*[43]	1981	DF–ESR	2.7×10^{-11}
Umemoto *et al.*[92]	1998	LP–LIF	2.1×10^{-11}

The recommended value is an average of the value reported by Fell *et al.*,[43] adjusted downwards by a factor of 0.6 (see the discussion in the introduction to this section), and of Umemoto *et al.*[92]

There are no product data. The reaction is probably insertion.

$N(^2D)+C_2F_6 \rightarrow$ products

Fell *et al.*,[43] using the discharge flow–electron spin resonance technique, reported a limiting value for the rate constant of $k \leqslant 10^{-14}$ cm^3 molecule^{-1} s^{-1}. There are no product data. The reaction is probably all physical quenching; there are no exothermic product channels.

$N(^2D)+C_3H_8 \rightarrow$ products

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Fell *et al.*[43]	1981	DF–ESR	4.6×10^{-11}
Umemoto *et al.*[92]	1998	LP–LIF	3.1×10^{-11}

The recommended value is an average of the value reported by Fell *et al.*,[43] adjusted downwards by a factor of 0.6 (see the discussion in the introduction to this section), and of Umemoto *et al.*[92]

There are no product data. The reaction is probably insertion.

$N(^2D)+n\text{-}C_4H_{10} \rightarrow$ products

The only measurement is by Fell *et al.*,[43] using the discharge flow–electron spin resonance technique. They reported $k=5.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1}; this has been adjusted downwards by a factor of 0.6 to obtain the recommended value (see the discussion in the introduction to this section). There are no product data. The reaction mechanism is probably insertion.

$N(^2D)+\text{neo-}C_5H_{12} \rightarrow$ products

The only measurement is by Fell *et al.*,[43] using the discharge flow–electron spin resonance technique. They reported $k=4.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1}; this has been adjusted downwards by a factor of 0.6 to obtain the recommended value (see the discussion in the introduction to this section). There are no product data. The reaction mechanism is probably insertion.

$N(^2D)+C_2H_4 \rightarrow$ products

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Black *et al.*[7]	1969	FP–CL	1.2×10^{-10}
Sugawara *et al.*[67]	1980	PR–RA	3.7×10^{-11}
Fell *et al.*[43]	1981	DF–ESR	8.3×10^{-11}

The recommended value is an average of the value reported by Sugawara *et al.*[67] and of Fell *et al.*,[43] the later adjusted downwards by a factor of 0.6 (see the discussion in the introduction to this section).

There are no product data. However, on the basis of a detailed *ab initio* study of the reaction, Takayanagi *et al.*[93] concluded that the primary product channel would lead to cyclic-$CH(N)CH_2+H$.

$N(^2D)+CH_2CF_2 \rightarrow$ products

The only measurement is by Fell *et al.*,[43] using the discharge flow–electron spin resonance technique. They reported $k=5.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1}; this has been adjusted downwards by a factor of 0.6 to obtain the recommended value (see the discussion in the introduction to this section). The reaction probably leads to products, but there are no data.

$N(^2D)+C_3H_6 \rightarrow$ products

The only measurement is by Fell *et al.*,[43] using the discharge flow–electron spin resonance technique. They reported $k=1.1\times10^{-10}$ cm^3 molecule^{-1} s^{-1}; this has been adjusted downwards by a factor of 0.6 to obtain the recommended value (see the discussion in the introduction to this section). The reaction probably leads to products, but there are no data.

$N(^2D)+C_2H_2 \rightarrow$ products

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Fell *et al.*[43]	1981	DR–ESR	1.1×10^{-10}
Takayanagi *et al.*[81]	1998	PR–RA	6.5×10^{-11}

Takayanagi *et al.*[81] measured the rate constants over the temperature range 223–293 K, and reported $k=1.6$

TABLE 4. Rate constants normalized to the average value for the reactions of $N(^2P)$ with selected reactants

Source	Year	H_2	O_2	NO	N_2O	CO_2
Husain *et al.*[52]	1972	0.36	1.63	1.12	3.84	
Husain *et al.*[14]	1974	0.23	0.92	1.06	0.06	0.52
Young and Dunn[86]	1975			0.93	0.03	0.66
Iannuzzi and Kaufman[39]	1980		1.24			
Sugawara *et al.*[67]	1980			0.89		
Umemoto *et al.*[70]	1985	1.70	0.89			1.83
Phillips *et al.*[45]	1987		0.64			
Piper[48]	1993		0.78			
Suzuki *et al.*[10]	1993	1.70				
Shihira *et al.*[11]	1994		0.89			

$\times 10^{-10} \exp(-270/T)$ cm^3 molecule^{-1} s^{-1}. They also studied the reaction with C_2D_2, and found $k = 1.4 \times 10^{-10} \times \exp(-240/T)$ cm^3 molecule^{-1} s^{-1}. Their measurements are the basis for the recommended value. The results of Fell *et al.*,[43] adjusted downwards by a factor of 0.6 (see the discussion in the introduction to this section) are in excellent agreement at 298 K.

There are no product data. However, Takayanagi *et al.*[81] have carried out *ab initio* calculations and indicate that the reaction proceeds by addition at the triple bond followed by decomposition of the initially formed intermediate. The most likely product channel gives H+NCCH. These authors quote unpublished experimental results in support of their conclusions.

$N(^2D)+CO \rightarrow$ products

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Black *et al.*[7]	1969	FP–CL	6×10^{-12}
Husain *et al.*[14]	1974	FP–RA	2.1×10^{-12}
Piper *et al.*[49]	1987	DF–RF	1.7×10^{-12}

The recommended value is an average of the results of Husain *et al.*[14] and Piper *et al.*[49] According to Donovan and Husain,[2] $N(^2D)+CO$ correlates with $NCO(X\,^2\Pi_i)$, facilitating physical quenching.

$N(^2D)+CO_2 \rightarrow NO+CO$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Black *et al.*[7]	1969	FP–CL	6×10^{-13}
Lin and Kaufman[44]	1971	DF–RA	5×10^{-13}
Husain *et al.*[14]	1974	FP–RA	1.8×10^{-13}
Fell *et al.*[43]	1981	DF–ESR	6.8×10^{-13}
Piper *et al.*[49]	1987	DF–RF	3.5×10^{-13}

The recommended rate constant at 298 K is an average of the values reported by Lin and Kaufman,[44] Husain *et al.*,[14] Fell *et al.*[43] (adjusted downwards by a factor of 0.6 to obtain the recommended value; see the discussion in the introduction to this section), and Piper *et al.*[49] The data of Husain *et al.*[14] are clearly anomalous (see Table 1).

Lin and Kaufman[44] measured the O atom yield from the reaction, and found 1.05 for each $N(^2D)$ reacted, close to the theoretical limit of 1.0, based on the probable mechanism: $N(^2D)+CO_2 \rightarrow NO+CO$, followed by $N+NO \rightarrow N_2+O$. This suggests that the reaction leads stoichiometrically to NO.

5. Reactions of $N(^2P)$

Rate constants are given here for a total of 24 reactions of $N(^2P)$. Even though the number of reactions of $N(^2P)$ included here is almost the same as the number of $N(^2D)$ reactions, that is a consequence of a large body of data from a single source (Umemoto *et al.*[70]); the number of publications is much smaller. In general, these reactions are slower than the comparable $N(^2D)$ reactions, probably reflecting a lack of available adiabatic paths.[2] The experimental methods have been discussed in Sec. 4.

As in the case of the reactions of $N(^2D)$, the internal consistency of measurements from a single study can be examined by comparing the normalized rate constants for the most widely studied reactions. This is shown in Table 4. The data base from which these values were derived is much smaller than the comparable data base in the case of the $N(^2D)$ reactions. About the only conclusion that can be drawn from this table is that the data reported in Husain *et al.*[52] may be high as they were in the case of the comparable $N(^2D)$ reactions. The other data sets are not extensive enough to draw any firm conclusions.

The large body of data obtained by means of the pulse radiolysis–resonance absorption technique (PR–RA)[67,70,81] which are taken near 10^5 Pa, agree in general with measurements taken at much lower pressure. However, in the case of the reaction with H_2, these results are about a factor of 10 higher, and a pressure effect has been suggested. See the discussion under $N(^2P)+H_2$.

Data for the slow reactions are in many cases badly scattered. In the case of the reactions of CO and CO_2, there are in each case measurements from three laboratories which

TABLE 5. Recommended values for the rate constants of the reactions of $N(^2P)$[a]

Reaction	A	E/R	$k(298)$	$f(298)$[b]	Notes
$N(^2P)+H_2 \rightarrow N+H_2$			2×10^{-15}	3	see text
$N(^2P)+O \rightarrow N(^4S,^2D)+O(^3P,^1D)$			2.7×10^{-11}	1.5	
$N(^2P)+O_2 \rightarrow O+NO$	3.1×10^{-12}	60	2.5×10^{-12}	1.3	200–300 K
$N(^2P)+NO \rightarrow$ products			2.9×10^{-11}	1.3	
$N(^2P)+N_2O \rightarrow$ products			5×10^{-14}	2	
$N(^2P)+N \rightarrow$ products			6×10^{-13}	3	
$N(^2P)+N_2 \rightarrow N+N_2$			5×10^{-17}	5	
$N(^2P)+CH_4 \rightarrow$ products	4.5×10^{-13}	490	8.8×10^{-14}	1.5	
$N(^2P)+C_2H_6 \rightarrow$ products			5.4×10^{-13}	2	
$N(^2P)+$cy-$C_3H_6 \rightarrow$ products			1.9×10^{-12}	2	
$N(^2P)+C_3H_8 \rightarrow$ products			1.9×10^{-12}	2	
$N(^2P)+n$-$C_4H_{10} \rightarrow$ products			2.7×10^{-12}	2	
$N(^2P)+$iso-$C_4H_{10} \rightarrow$ products			3.5×10^{-12}	2	
$N(^2P)+$neo-$C_5H_{12} \rightarrow$ products			3.4×10^{-12}	2	
$N(^2P)+C_2H_4 \rightarrow$ products			3.0×10^{-11}	1.5	
$N(^2P)+CH_2CHF \rightarrow$ products			3.1×10^{-11}	2	
$N(^2P)+CH_2CF_2 \rightarrow$ products			6.4×10^{-12}	2	
$N(^2P)+CHFCHF \rightarrow$ products			3.1×10^{-11}	2	
$N(^2P)+CHFCF_2 \rightarrow$ products			2.3×10^{-11}	2	
$N(^2P)+C_2F_4 \rightarrow$ products			2.4×10^{-11}	2	
$N(^2P)+C_2H_2 \rightarrow$ products	1.0×10^{-10}	440	2.3×10^{-11}	2	200–300 K
$N(^2P)+CO \rightarrow$ products			6×10^{-15}	2	
$N(^2P)+CO_2 \rightarrow$ products			2×10^{-15}	2	
$N(^2P)+Cl_2 \rightarrow$ products			2.4×10^{-11}	2	

[a] Preexponential factors, A, and rate constants, $k(298)$, in units of $cm^3\ molecule^{-1}\ s^{-1}$; E/R in units of K.
[b] Multiplicative error factor. Applies to 298 K values only. Error limits are larger at lower or higher temperatures.

show moderate agreement for the CO_2 reaction and serious disagreement for the CO reaction. There is no obvious basis for the agreement or disagreement.

A major problem in studying slow reactions arises from impurity effects or secondary reactions. Reactive impurities will lead to measured rate constants that are too high. However, if significant amounts of ground state nitrogen atoms, $N(^4S)$, and excited molecular nitrogen, $N_2(A\ ^3\Sigma_u^+)$, are present, $N(^2P)$ may be generated through the reaction $N_2(A\ ^3\Sigma_u^+)+N(^4S) \rightarrow N_2+N(^2P)$, leading to a measured rate constant which is too low. In the absence of additional information, it is not possible to know which sets of data are the most reliable. Recommended values for the rate constants of the reactions of $N(^2P)$ are given in Table 5.

$N(^2P)+H_2 \rightarrow N+H_2$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Husain *et al.*[52]	1972	FP-RA	3.0×10^{-15}
Husain *et al.*[14]	1974	FP-RA	1.9×10^{-15}
Young and Dunn[86]	1975	DF-ES	$\leq 8\times10^{-16}$
Umemoto *et al.*[70]	1985	PR-RA	1.4×10^{-14}
Suzuki *et al.*[10]	1993	PR-RA	1.4×10^{-14}

Suzuki *et al.*[10] studied the reaction over the temperature range 213–300 K, and reported $k=3.5\times10^{-13}\exp(-950/T)\ cm^3\ molecule^{-1}\ s^{-1}$. For the comparable reaction with D_2, they give $k=1.9\times10^{-13}\exp(-930/T)\ cm^3\ molecule^{-1}\ s^{-1}$.

The recommended value for the rate constant at 298 K is based on the data of Husain *et al.*[14] taken at low pressure. The experiments of Umemoto *et al.*[70] and of Suzuki *et al.*[10] were carried out near atmospheric pressure which may explain why they differ so greatly from the data obtained at lower pressure. Note that in the case of the comparable reactions involving $N(^2D)$ there is no great disparity between low and high pressure results. Caution should be used in applying the low pressure numbers to high pressure systems. Until the problem can be resolved, no recommendations can be made for the temperature coefficients.

The reaction is probably predominantly quenching to $N(^2D)$, at least at low pressure. See Donovan and Husain[2] for a discussion of the allowed paths.

$N(^2P)+O \rightarrow N(^4S,^2D)+O(^3P,^1D)$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Young and Dunn[86]	1975	DF-ES	1.0×10^{-11}
Piper[48]	1993	DF-RF	2.7×10^{-11}

The recommended value is taken from Piper.[48]

This is one of the few reactions of excited nitrogen atoms in which the $N(^2P)$ reaction is faster than the $N(^2D)$ reaction (see Table 2). The reaction is sufficiently energetic to yield products in excited states. However, there are no data on product yields. There is evidence that NO^+ is a chemi-ionization product.[48]

$N(^2P)+O_2 \rightarrow O+NO$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Husain *et al.*[52]	1972	FP–RA	4.6×10^{-12}
Husain *et al.*[14]	1974	FP–RA	2.6×10^{-12}
Young and Dunn[86]	1975	DF–ES	$\leq 2\times10^{-12}$
Iannuzzi and Kaufman[39]	1980	DF–RF	3.5×10^{-12}
Umemoto *et al.*[70]	1985	PR–RA	2.5×10^{-12}
Phillips *et al.*[45]	1987	DF–LPI	1.8×10^{-12}
Piper[48]	1993	DF–RF	2.2×10^{-12}
Shihira *et al.*[11]	1994	PR–RA	2.5×10^{-12}

The earlier results of Husain *et al.*[52] are discounted. The recommended room temperature rate constant is an average of the balance of the data (not including the limiting value).

Shihira *et al.*[11] studied the reaction over the temperature range 210–295 K, and reported $k=3.1\times10^{-12} \times\exp(-60/T)$ cm^3 $molecule^{-1}$ s^{-1}. The recommended temperature coefficients are based on their results adjusted to the recommended value at 298 K.

There are no quantitative data on product yields. However, NO has been observed as a product. Rawlins *et al.*[46] measured the initial vibrational state distribution of the product $NO(X\,^2\Pi)$ at 100 K. They inferred that the branching ratios for formation of $O(^1S)$, $O(^1D)$ and $O(^3P)$ were about equal at that temperature. They suggest that the reaction may proceed through a long lived reaction complex, possibly involving insertion.

$N(^2P)+NO \rightarrow$ products

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Husain *et al.*[52]	1972	FP–RA	3.4×10^{-11}
Husain *et al.*[14]	1974	FP–RA	3.2×10^{-11}
Young and Dunn[86]	1975	DF–ES	2.8×10^{-11}
Sugawara *et al.*[67]	1980	PR–RA	2.7×10^{-11}

The earlier value of Husain *et al.*[52] is discounted; the recommended value is the average of the last three entries.

There are no exothermic adiabatic paths to products. Physical quenching is probably the only process.[2]

$N(^2P)+N_2O \rightarrow N_2+NO$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Husain *et al.*[52]	1972	FP–RA	3.4×10^{-12}
Husain *et al.*[14]	1974	FP–RA	5×10^{-14}
Young and Dunn[86]	1975	DF–ES	2.5×10^{-14}
Umemoto *et al.*[70]	1985	PR–RA	6.7×10^{-14}

The earlier value of Husain *et al.*[52] is discounted; the recommended value is the average of the last three entries. The agreement is poor.

The reaction to produce NO is strongly exothermic. Husain *et al.*[14] concluded that the mechanism involved formation of excited states of NO and that the low reactivity was the consequence of an energy barrier leading to such states.

$N(^2P)+N \rightarrow$ products

The only data are from a discharge flow–emission spectroscopy study of Young and Dunn,[86] who reported $k=6.2\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. There is a high degree of uncertainty in this measurement because of the experimental difficulty.

$N(^2P)+N_2 \rightarrow N+N_2$

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Lin and Kaufman[44]	1971	DF–RA	6×10^{-14} (400 K)
Husain *et al.*[52]	1972	FP–RA	$\leq 3\times10^{-16}$
Husain *et al.*[14]	1974	FP–RA	1×10^{-16}
Sugawara *et al.*[67]	1980	PR–RA	3.3×10^{-17}
Umemoto *et al.*[70]	1985	PR–RA	$\leq 4\times10^{-16}$

Note that the rate constant of Lin and Kaufman[44] was measured at 400 K. Even allowing for the temperature difference between these and other workers, the data are badly scattered. The lower values are preferred. The recommended value at 298 K is based on the data of Sugawara *et al.*[67] and assigned a large uncertainty.

$N(^2P)+CH_4 \rightarrow$ products

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Umemoto *et al.*[70]	1985	PR–RA	7.8×10^{-14}
Takayanagi *et al.*[90]	1999	PR–RA	9.3×10^{-14} (292 K)

Takayanagi *et al.*[90] studied the reaction over the temperature range 223–292 K, and derived the rate expression $k=5.0\times10^{-13}\exp(-490/T)$ cm^3 $molecule^{-1}$ s^{-1}. They also measured the rate constant for the reaction with CD_4 to be $k = 3.1\times10^{-13}\exp(-480/T)$ cm^3 molecule^{-1} s^{-1}.

The recommended rate constant at 298 K is an average of the two reported values (at 298 K). The recommended temperature coefficients are based on the recommended value at 298 K and the temperature dependence of Takayanagi *et al.*[90]

There are no product data, although physical quenching may be dominant.[70,90]

$N(^2P)+C_2H_6\rightarrow$products

The only measurement is by Umemoto *et al.*,[70] using the pulse radiolysis–resonance absorption technique. They reported $k=5.4\times10^{-13}$ cm^3 molecule^{-1} s^{-1}. There are no product data.

$N(^2P)+$cy-$C_3H_6\rightarrow$products

The only measurement is by Umemoto *et al.*,[70] using the pulse radiolysis–resonance absorption technique. They reported $k=1.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. There are no product data.

$N(^2P)+C_3H_8\rightarrow$products

The only measurement is by Umemoto *et al.*,[70] using the pulse radiolysis–resonance absorption technique. They reported $k=1.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. There are no product data.

$N(^2P)+$n-$C_4H_{10}\rightarrow$products

The only measurement is by Umemoto *et al.*,[70] using the pulse radiolysis–resonance absorption technique. They reported $k=2.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. There are no product data.

$N(^2P)+$iso-$C_4H_{10}\rightarrow$products

The only measurement is by Umemoto *et al.*,[70] using the pulse radiolysis–resonance absorption technique. They reported $k=3.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. There are no product data.

$N(^2P)+$neo-$C_5H_{12}\rightarrow$products

The only measurement is by Umemoto *et al.*,[70] using the pulse radiolysis–resonance absorption technique. They reported $k=3.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. There are no product data.

$N(^2P)+C_2H_4\rightarrow$products

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Sugawara *et al.*[67]	1980	PR–RA	2.8×10^{-11}
Umemoto *et al.*[70]	1985	PR–RA	3.2×10^{-11}

These measurements are from the same laboratory. The recommended value is the average of these. The reaction probably involves product formation rather than physical quenching, but there are no data.

$N(^2P)+CH_2CHF\rightarrow$products

The only measurement is by Umemoto *et al.*,[70] using the pulse radiolysis–resonance absorption technique. They reported $k=3.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. There are no product data.

$N(^2P)+CH_2CF_2\rightarrow$products

The only measurement is by Umemoto *et al.*,[70] using the pulse radiolysis–resonance absorption technique. They reported $k=6.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. There are no product data.

$N(^2P)+CHFCHF\rightarrow$products

The only measurement is by Umemoto *et al.*,[70] using the pulse radiolysis–resonance absorption technique. They reported $k=3.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. There are no product data.

$N(^2P)+CHFCF_2\rightarrow$products

The only measurement is by Umemoto *et al.*,[70] using the pulse radiolysis–resonance absorption technique. They reported $k=2.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. There are no product data.

$N(^2P)+C_2F_4\rightarrow$products

The only measurement is by Umemoto *et al.*,[70] using the pulse radiolysis–resonance absorption technique. They reported $k=2.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. There are no product data.

$N(^2P)+C_2H_2\rightarrow$products

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Umemoto *et al.*[70]	1985	PR–RA	3.2×10^{-11} (295 K)
Takayanagi *et al.*[81]	1998	PR–RA	2.3×10^{-11}

Takayanagi *et al.*,[81] who studied the reaction over the temperature range 223–293 K, reported $k=1.0\times10^{-10}\times\exp(-440/T)$ cm^3 molecule^{-1} s^{-1}. They also studied the comparable reaction with C_2D_2 and reported $k=7.1\times10^{-11}\times\exp(-380/T)$ cm^3 molecule^{-1} s^{-1}.

The two measurements (from the same laboratory) are in good agreement. The recommended value is based on the results of Takayanagi *et al.*[81]

The relatively large rate constant suggests that chemical reaction is dominant, but there are no product data (see the discussion in Refs. 70 and 81).

$N(^2P)+CO \rightarrow$ products

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Husain *et al.*[14]	1974	FP–RA	9.0×10^{-13}
Young and Dunn[86]	1975	DF–ES	$\leq7\times10^{-15}$
Umemoto *et al.*[70]	1985	PR–RA	6.5×10^{-15}

The disagreement is inexplicable, and indicates a major source of error in one or more experiments. The very high value of Husain *et al.*[14] is rejected. The recommended value is based on the data of Umemoto *et al.*[70]

There are no product data. The mechanism may involve relaxation to $N(^2D)$.[2]

$N(^2P)+CO_2 \rightarrow$ products

The rate constant data are summarized in the following table:

Source	Year	Method	k (298 K)
Husain *et al.*[14]	1974	FP–RA	1.1×10^{-15}
Young and Dunn[86]	1975	DF–ES	1.4×10^{-15}
Umemoto *et al.*[70]	1985	PR–RA	3.9×10^{-15}

The recommended value is based on the data of Umemoto *et al.*[70] (compare these results with those for the CO reaction).

There are no product data.

$N(^2P)+Cl_2 \rightarrow$ products

The only measurement is by Umemoto *et al.*,[70] using the pulse radiolysis–resonance absorption technique. They reported $k=2.4\times10^{-11}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$. There are no product data.

6. Reactions of $N_2(A\,^3\Sigma_u^+)$

Rate constant data are provided here for 76 reactions of $N_2(A\,^3\Sigma_u^+)$. The data are given in three tables: reactions of compounds containing H, O, and N; reactions of compounds containing C; and reactions of miscellaneous compounds.

Following each summary table, each reaction is discussed in detail. The literature values of rate constants are presented in tabular format in many cases. If there are measurements of the rate constants as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$, the data are given in tabular form for $v=0-v=6$. These vibrational levels ($v=0-v=6$) lie below the onset of the $N_2(B\,^3\Pi_g)$ state. If data are reported for $v\geq7$, they are given in the text. Recommended values given in the summary tables are for nominal $N_2(A\,^3\Sigma_u^+, v=0)$. In some cases, the vibrational level of the $N_2(A\,^3\Sigma_u^+)$ molecule is not known or specified. Depending on experimental conditions, one can have significant levels of $v>0$. If not specified, the reported rate constants are given in the $v=0$ column, but the actual measurements may be for some mix of vibrational levels.

As noted in Sec. 2, the only exception to this format is Table 9, which compiles data on a broad range of species, mostly the results of single measurements. For these data, the rate constants are tabulated at 298 K for $v=0$ and $v=1$. If there are more than one measurement a recommended value may also be provided. If there are product data or information on other aspects of the reaction, this is discussed in a footnote to the table.

From the point of view of modeling applied systems, one is interested in two classes of reaction of $N_2(A\,^3\Sigma_u^+)$: reactions which attenuate $N_2(A\,^3\Sigma_u^+)$, and reactions of additive species which are transformed (destroyed) by reaction with $N_2(A\,^3\Sigma_u^+)$. In the first category are the atmospheric gases, N_2, O_2, H_2O, N, and O. In the latter category are oxides of nitrogen and sulfur, hydrocarbons, fluorocarbons and volatile organic compounds of all kinds.

Ideally, it would be desirable to know the rate constants for reaction for a range of anticipated vibrational levels for $N_2(A\,^3\Sigma_u^+)$, distinguishing between vibrational relaxation and electronic quenching, which in many cases leads to dissociation. However, it is difficult to always distinguish between these.

To try and keep terms clear, quenching will always refer to electronic quenching of $N_2(A\,^3\Sigma_u^+, v=n)$ to the ground electronic state $N_2(^1\Sigma_g^+, v=n')$, irrespective of the vibrational levels of either. Relaxation will refer to vibrational relaxation of $N_2(A\,^3\Sigma_u^+ v=n)$ resulting in formation of $N_2(A\,^3\Sigma_u^+ v=n')$, where $n-n'$ is expected to be 1 or 2. The measured rate constant refers to the overall process without distinguishing between possible mechanisms.

As in the case of the reactions of the excited atomic states of nitrogen, the internal consistency of measurements from a single study can be examined by comparing the normalized rate constants for the most widely studied reactions. This is shown in Table 6. Although only qualitative conclusions can be drawn, the values in Table 6, suggest that the data of Black *et al.*[7] and of Clark and Setser[56] are too high. This also appears to be the case with the data of Meyer *et al.*,[57] except that their results for the NO reaction are sharply lower than the average values. Thus, although differences in results may depend in some cases on broad factors such as the method for the measurement of time, in other cases the disagreements may arise from very specific errors in experimental execution. Both kinds of problem represent unknowns to the evaluator.

Although there are a variety of methods available to make and monitor $N_2(A\,^3\Sigma_u^+)$, most of the data reported here were obtained using some kind of discharge flow system. Other methods which have been used in a number of studies include flash photolysis and pulse radiolysis. These are discussed in more detail by Golde.[4] A critique of experimental methods is given by Piper *et al.*[23]

There are basically two approaches to discharge flow sources. In one, $N_2(A\,^3\Sigma_u^+)$ is formed in a discharge in N_2 or mixtures of N_2 in He or Ar. This kind of source leads to the

TABLE 6. Rate constants normalized to the average value for the reactions of $N_2(A\ ^3\Sigma_u^+,\ v=0)$ with selected reactants

Source	Year	H_2	NH_3	O_2	NO	N_2O	C_2H_4	CO	CO_2
Black *et al.*[7]	1969	0.90			1.31	1.40	1.02	1.21	1.67
Young *et al.*[59]	1969		1.30	0.95	1.15	0.90	1.27	0.92	
Callear and Wood[22]	1971	0.90		1.18	1.31	0.86	0.93	0.73	
Meyer *et al.*[57]	1971		1.16	2.14	0.23		1.35		
Slanger *et al.*[36]	1973	0.57	0.94	1.08		0.90		0.82	
Dreyer and Perner[66]	1973				0.46		0.54		
Dreyer *et al.*[12]	1974		0.59	0.62	0.46			0.87	0.33
Dunn and Young[76]	1976			0.95					
Mandl and Ewing[78]	1977				0.70				
Levron and Phelps[25]	1978	0.72							
Clark and Setser[56]	1980			1.48	2.46	1.08	1.02	2.42	
Zipf[38]	1980			0.62					
Piper *et al.*[23]	1981			0.78					
Iannuzzi and Kaufman[13]	1981			0.82					
Shibuya *et al.*[28]	1984				1.13				
Thomas and Kaufman[8]	1985			0.82					
Cao and Setser[27]	1985			1.02			1.02		
DeSousa *et al.*[16]	1985			0.82					
Piper *et al.*[20]	1986				1.08				
Thomas *et al.*[51]	1987			0.82	0.92	0.87	0.85	0.73	
Hack *et al.*[53]	1988	1.15	1.01						
Bohmer and Hack[15]	1989	1.75							
Golde *et al.*[61]	1989			0.72					
Ho and Golde[61]	1991						1.02		
Suzuki *et al.*[64]	1993			0.83				0.29	
Suzuki *et al.*[54]	1997				0.79				

formation of many excited species other than $N_2(A\ ^3\Sigma_u^+)$ as well as to copious amounts of ground state N atoms which rapidly remove $N_2(A\ ^3\Sigma_u^+)$ (see the section below on the $N_2(A\ ^3\Sigma_u^+)+N$ reaction for which $k=4.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1}). To reduce the effect of N atoms, a dilute mixture of N_2 in He or Ar can be used.

An alternative to that approach was developed by Setser and co-workers[89] in which one started by exciting argon (or xenon or krypton) in a discharge to the first metastable state, which in turn was allowed to react with N_2. The initial products of that interaction are rapidly transformed to $N_2(A\ ^3\Sigma_u^+)$ with excitation of vibrational levels up to at least $v=6$. From a practical point of view, this approach is only feasible under flow conditions using argon as the initiator. The great advantage of the method is that nitrogen atoms are only a minor product (probably less that 5%[4]), so that loss due to reactions of N atoms is minimized.

In the flash photosensitization technique of Callear and Wood[22] the excited species is produced from photolytically excited xenon or krypton in the absence of significant amounts of N atoms. The direct vacuum ultraviolet photolysis of N_2O (see for example Young *et al.*[59]) has also been used, but is somewhat less desirable since N atoms are also generated.

Pulse radiolysis techniques have been applied by Dreyer and Perner.[12,66] In this method reactions can be studied over a broad range of pressure (over 10^5 Pa if desired). However, their rate constants appear to be low compared to the consensus values; adjustment upwards by a factor of about 1.5–2.0 is appropriate. However, this is not universally true (see the data for the CO reaction).

In all these approaches, $N_2(A\ ^3\Sigma_u^+)$ is generated as a mix of vibrational levels. For kinetics applications, we want to know the rate constants with reference to specific vibrational levels. Thus, the monitoring method is the critical factor. Some of the earlier measurements (see for example Refs. 7, 22, and 36) involved the use of some form of sensitized fluorescence to monitor the $N_2(A\ ^3\Sigma_u^+)$; e.g., the reaction $N_2(A\ ^3\Sigma_u^+)+NO\rightarrow N_2+NO(A\ ^2\Sigma^+)$, for which one can measure the emission from the decay of $NO(A\ ^2\Sigma^+)$. Such methods are not sensitive to the vibrational level of the $N_2(A\ ^3\Sigma_u^+)$. The most straightforward method is to monitor the Vegard–Kaplan $N_2(A,v-X)$ emission. However, the emission is weak and not really usable much beyond $v=1$. More general methods involve using laser induced fluorescence using the $N_2(B\leftarrow A)$ system, or visible absorption to $N_2(B\ ^3\Pi_g)$.

Suzuki *et al.*[54,64] describe a method in which it was postulated that $N_2(A\ ^3\Sigma_u^+)$ could be formed in a pulsed discharge and its concentration followed by measuring the electron current generated when the excited species collided with an electrode. The method does not appear to be specific to $N_2(A\ ^3\Sigma_u^+)$, and the reported rate constants are suspect. Recommended values for the rate constants of the reactions of $N_2(A\ ^3\Sigma_u^+)$ are given in Tables 7–9.

In summarizing the status of our knowledge regarding mechanism, Golde[4] argued that there is only one mechanism for quenching, electronic to electronic energy transfer to an excited state of the collision partner, which can then decompose. It now seems clear that although the energy of the $N_2(A\,^3\Sigma_u^+)$ species above the ground state is about 6.2 eV, it is not necessarily available for furthering chemical reaction. Reaction may be dependent on the acceptor species having triplet electronic states available at or below about 6 eV, particularly if the excited state is dissociative. Vibrational excitation of $N_2(A\,^3\Sigma_u^+)$ may help in accessing such states.

A major problem in using the kinetics data given here is the lack of even qualitative data on products or their yields, particularly for organic species. Reactions of alkenes or alkynes are fast, and almost certainly involve chemical transformations, yet the mechanisms are not known. For ethylene it is known that molecular elimination of H_2 is important, with a minor channel leading to H atoms. For the higher alkenes there is some data indicating an H atom channel for C_3H_6 and cis-2-C_4H_8. There are no product data for C_2H_2 or for most alkanes or haloalkanes.

It should also be noted, that even if vibrational relaxation is indicated as a major path in a given reaction, that does not rule out electronic and dissociative quenching as an important process. Thus some caution must be used in interpreting what limited information is available on reaction paths.

$N_2(A\,^3\Sigma_u^+)+H\rightarrow$products
$N_2(A\,^3\Sigma_u^+)+H\rightarrow N_2+H$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-10}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

Source	Year	Method	0	1
Dunn and Young[76]	1976	DF–ES	0.035	0.035
Hovis and Whitefield[79]	1987	DF–ES	0.5	
Ho and Golde[61]	1991	DF–ES	2.1	

In a curious reversal of the temporal nature of rate constants, the value is seen to be increasing with time. The measurements are difficult because of the need to measure the H atom concentration at low levels in a complex reaction system. Dunn and Young[76] and Hovis and Whitefield[79] measured the H atom concentration using a titration technique, while Ho and Golde[61] used the resonance fluorescence technique. The latter is the more reliable approach, and the data of Ho and Golde[61] are the basis for the recommendation.

Ho and Golde[61] found that the yield of NH was less than 1% of the total reaction. This agrees with the observation of Hack *et al.*[53] in their study of the $N_2(A\,^3\Sigma_u^+)+H_2$ reaction, in which addition of H atoms did not enhance the observed NH signal, although it attenuated that of $N_2(A\,^3\Sigma_u^+)$. The reaction mechanism is probably all quenching (possibly through an excited state of N_2H); the product $N_2(X)$ ground state may be vibrationally excited. Sperlein and Golde[62] have carried out a detailed theoretical study of the reaction in order to explain the very efficient quenching.

$N_2(A\,^3\Sigma_u^+)+H_2\rightarrow N_2+2H$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-15}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

Source	Year	Method	0	1	2	3	4	5	6
Black *et al.*[7]	1969	FP–CL	3						
Young *et al.*[59]	1969	P–CL	≤7						
Callear and Wood[22]	1971	FP–CL	3						
Slanger *et al.*[36]	1973	FP–CL	1.9						
Levron and Phelps[25]	1978	PD–ES	2.4	44					
Hack *et al.*[53]	1988	DF–LIF	3.8	22	23	25			
Bohmer and Hack[15]	1989	DF–LIF	5.8	17	18	20			
Golde *et al.*[55]	1989	DF–LIF			59	160	280	540	1000

The agreement is only fair. The data of Black *et al.*,[7] Young *et al.*,[59] and Callear and Wood[22] are discounted. The recommended rate constant at 298 K for $v=0$ is an average of the data from Refs. 36, 25, 53 and 15.

Slanger *et al.*[36] studied the reaction over the temperature range 240–370 K, and report $k=2.2\times10^{-10}\exp(-3500/T)$ $\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

The recommended temperature coefficients given in Table 7 are based on the recommended value for the rate constant at 298 K and the temperature dependence reported by Slanger *et al.*[36]

There are serious disagreements for the rate constants at higher vibrational levels. Thus, while Hack *et al.*[53] and Bohmer and Hack[15] observe a leveling off of rate constants beyond $v=1$, Golde *et al.*,[55] who interpreted their data in terms of electronic quenching, see a continuous rise. They

TABLE 7. Recommended values for the rate constants of the reactions of $N_2(A\ ^3\Sigma_u^+)$ with species containing H, O and N[a]

Reaction	A	E/R	$k(298)$	$f(298)$[b]	Notes
$N_2(A\ ^3\Sigma_u^+)+H\rightarrow$products			2.1×10^{-10}	1.5	
$N_2(A\ ^3\Sigma_u^+)+H_2\rightarrow N_2+2H$	4.4×10^{-10}	3500	3.5×10^{-15}	2	240–370 K
$N_2(A\ ^3\Sigma_u^+)+OH\rightarrow N_2+OH(A\ ^2\Sigma^+)$			1.0×10^{-10}	1.3	
$N_2(A\ ^3\Sigma_u^+)+H_2O\rightarrow N_2+H+OH$			5×10^{-14}	2	
$N_2(A\ ^3\Sigma_u^+)+NH_3\rightarrow N_2+H+NH_2$			1.2×10^{-10}	1.5	
$N_2(A\ ^3\Sigma_u^+)+HN_3\rightarrow$products			7.0×10^{-11}	1.5	
$N_2(A\ ^3\Sigma_u^+)+NH_2OH\rightarrow N_2+NH_2+OH$			1.7×10^{-10}	2	
$N_2(A\ ^3\Sigma_u^+)+O\rightarrow N_2+O$			2.5×10^{-11}	1.3	
$N_2(A\ ^3\Sigma_u^+)+O_2\rightarrow$products	$k=k(300)\times(T/300)^{0.55}$		2.5×10^{-12}	1.2	80–560 K; see text
$N_2(A\ ^3\Sigma_u^+)+O_2(^1\Delta_g)\rightarrow N_2+2O$			$\leq2\times10^{-11}$		
$N_2(A\ ^3\Sigma_u^+)+O_3\rightarrow$products			4.2×10^{-11}		
$N_2(A\ ^3\Sigma_u^+)+NO\rightarrow N_2+NO(A\ ^2\Sigma^+)$			6.4×10^{-11}	1.3	
$N_2(A\ ^3\Sigma_u^+)+N_2O\rightarrow$products	9.3×10^{-12}	120	6.2×10^{-12}	1.3	240–370 K
$N_2(A\ ^3\Sigma_u^+)+NO_2\rightarrow N_2+NO(X\ ^2\Pi)+O$			1.3×10^{-11}	2	
$N_2(A\ ^3\Sigma_u^+)+N\rightarrow N_2+N(^2P)$			4.4×10^{-11}	1.5	
$N_2(A\ ^3\Sigma u+)+N_2\rightarrow N_2+N_2$			$\leq3\times10^{-18}$		
$N_2(A\ ^3\Sigma_u^+)+N_2(A\ ^3\Sigma_u^+)\rightarrow N_2+N_2(B\ ^3\Pi_g)$			4×10^{-10}		see text

[a]Preexponential factors, A, and rate constants, $k(298)$, in units of cm^3 molecule^{-1} s^{-1}; E/R in units of K.
[b]Multiplicative error factor. Applies to 298 K values only. Error limits are larger at lower or higher temperatures.

show data plots for $v=3$, 5, and 6, which are clearly linear over the range of their experiments, indicating that vibrational relaxation was not important under their conditions. Bohmer and Hack[15] show data plots for $v=0-v=3$. Their data are increasingly scattered going to higher vibrational levels and could be interpreted in terms of larger rate constants. This is the only case in which a great disparity in rate constants as a function of vibrational level has been reported.

Bohmer and Hack[15] have measured product yields. The yield of H atoms is directly proportional to the amount of added H_2. Although this is a major and possibly only product, it was not determined quantitatively. They argue that the enhancement in rate going from $v=0$ to $v=1$ is due to reactive quenching, not to vibrational relaxation as suggested by Levron and Phelps.[25]

Sperlein and Golde[75] on the basis of an *ab initio* study, deduced a barrier for reaction of about 49 kJ mol^{-1}, which is compatible with the measured activation energy. It is probable that vibrational energy can be used at least in part to overcome the barrier.

$N_2(A\ ^3\Sigma_u^+)$+OH→products
$N_2(A\ ^3\Sigma_u^+)$+OH→OH$(A\ ^2\Sigma^+)$+N_2

Ho and Golde,[61] using the discharge flow–emission spectroscopy technique combined with resonance florescence to monitor OH radicals, reported the total rate constant to be $k=1.1\times10^{-10}\,cm^3$ molecule^{-1} s^{-1}. For the channel leading to OH$(A^2\Sigma^+)$, they reported $k=1.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, in agreement with the value reported by Wategaonkar and Setser[60] of $k=0.95\times10^{-10}$ cm^3 molecule^{-1} s^1.

The reaction forming OH$(A\ ^2\Sigma^+)$ is thus the dominant and possibly only channel.

$N_2(A\ ^3\Sigma_u^+)+H_2O\rightarrow N_2+H+OH$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\ ^3\Sigma_u^+)$. Rate constants in units of $10^{-12}\,cm^3$ molecule^{-1} s^{-1}.

Source	Year	Method	0	1	2	3	4	5	6
Callear and Wood[80]	1971	FP-CL	0.055						
Golde *et al.*[55]	1989	DF–LIF					37	45	56

The only measurements for $v=0$ are from Callear and Wood.[80]

Golde *et al.*[55] have detected OH by LIF, and indicate that this is a major product. However, there are no quantitative yield data.

$N_2(A\ ^3\Sigma_u^+)+NH_3\rightarrow N_2+H+NH_2$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\ ^3\Sigma_u^+)$. Rate constants in units of $10^{-10}\,cm^3$ molecule^{-1} s^{-1}.

Source	Year	Method	0	1	2	3	4	5	6
Young *et al.*[59]	1969	P–CL	1.8						
Callear and Wood[22]	1971	FP–CL	≤0.2						
Meyer *et al.*[57]	1971	DF–CL	1.6						
Slanger *et al.*[36]	1973	FP–CL	1.3						
Dreyer *et al.*[12]	1974	PR–AS	0.82	0.86	1.5	1.2	1.6	1.5	2.3
Hack *et al.*[53]	1988	DF–LIF	1.4	1.5	1.8	2.3			

Dreyer *et al.*[12] also reported rate constants for $v=7$ of $0.45\times10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ and for $v=8$ of $1.1\times10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$.

The recommended value at 298 K is the average of the data given by Slanger *et al.*,[36] Dreyer *et al.*,[12] and Hack *et al.*[53] The data of Callear and Wood[22] are in significant disagreement, indicating some source of unrecognized systematic error.

There have been three studies of product yields. Golde and Moyle[32] found that H atoms were a major product, and the yield was independent of added CF_3H, which brings about vibrational relaxation of $N_2(A\,^3\Sigma_u^+,v)$. Under their experimental conditions, the initial distribution of $v=0$, 1, 2, and 3 was 1.0, 0.48, 0.19, and 0.14, respectively. They concluded that the rate constants and branching fraction for dissociation were independent of v. They also argued that the low values for the rate constants reported by Dreyer *et al.*[12] for $v=0$ and 1 are in error. Hack *et al.*[53] measured the yield of NH_2, and concluded that the major channel was to produce $H+NH_2+N_2$, with possibly 10% going to a second channel $NH+H_2+N_2$. Tao *et al.*[65] measured the branching ratio for the channel going to $H+NH_2+N_2$ to be 0.9 ± 0.2. It is likely that this is the only major channel.

$N_2(A\,^3\Sigma_u^+)+HN_3\rightarrow NH+2N_2$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$.

Source	Year	Method	0	1	2	3
Cao and Setser[82]	1988	DF–ES	8.5			
Bohmer and Hack[34]	1991	DF–LIF	5.5	5.5	5.2	7.3

The recommended value is the average of the two reported measurements.

The branching ratio to form $NH(A\,^3\Pi)$ has been reported as 0.025.[82] Although dissociative quenching is probably the major path, there are no quantitative data on product yields.

$N_2(A\,^3\Sigma_u^+)+NH_2OH\rightarrow NH_2+OH+N_2$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$.

Source	Year	Method	0	1	2	3
Bohmer and Hack[34]	1991	DF–LIF	1.7	2.3	4.0	4.0

Bohmer and Hack[34] also measured the yield of NH_2 and OH by LIF, and reported a branching ratio for $NH_2=0.9\pm0.1$.

$N_2(A\,^3\Sigma_u^+)+O\rightarrow N_2+O$
$N_2(A\,^3\Sigma_u^+)+O\rightarrow N_2+O(^1S)$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$.

Source	Year	Method	0	1	2	3	4	5	6
Meyer *et al.*[58]	1970	DF–CL/ES	2						
Dunn and Young[76]	1976	DF–ES	1.5	1.5					
Piper *et al.*[18]	1981	DF–ES	2.8	3.4					
Thomas and Kaufman[8]	1985	DF–LIF	3.5	4.1	4.6	5.2			
De Souza *et al.*[5]	1985	DF–ES	2.1						
De Benedictis and Dilecce[29]	1997	DF–LIF			3.3	3.5	2.1	4.3	4.6

De Benedictis and Dilecce[29] also reported for $v=7$, $k=7.4\times10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. The data from Meyer *et al.*[58] were measured relative to the rate constant for the O_2 reaction for which they found $k(O)/k(O_2)=3-4$. Using the recommended value for O_2 from this evaluation gives $k(O)=0.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. These data are discounted. The recommended rate constant at 298 K is the average of the rate constants given in Refs. 76, 18, 8 and 5.

Piper[17] has measured the rate constant for excitation of $O(^1S)$ in the reaction for $v=0$, and reported $k=2.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. Using a value for the total rate constant measured earlier in the same laboratory (Piper *et al.*[18]), Piper[17] deduced that the branching ratio for the $O(^1S)$ channel is 0.75 ± 0.13. There is no evidence for a channel leading to NO.

$N_2(A\,^3\Sigma_u^+)+O_2\rightarrow$products
$N_2(A\,^3\Sigma_u^+)+O_2\rightarrow N_2+2O$
$N_2(A\,^3\Sigma_u^+)+O_2\rightarrow N_2O+O$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of 10^{-12} cm^3 molecule^{-1} s^{-1}.

Source	Year	Method	0	1	2	3	4	5	6
Young *et al.*[59]	1969	P–CL	2.9						
Callear and Wood[22]	1971	FP–CL	3.6						
Meyer *et al.*[57]	1971	DF–CL	6.5						
Slanger *et al.*[36]	1973	FP–CL	3.3						
Dreyer *et al.*[12]	1974	PR–AS	1.9	7.4	5.0	3.4	6.2	5.8	6.5
Dunn and Young[76]	1976	DF–ES	2.9	2.9					
Clark and Setser[56]	1980	DF–ES	4.5	5.1					
Zipf[38]	1980	PD–ES	1.9	4.0					
Piper *et al.*[23]	1981	DF–ES	2.3	4.1					
Iannuzzi and Kaufman[13]	1981	DF–LIF	2.5	3.9	4.3				
Thomas and Kaufman[8]	1985	DF–LIF	2.5	4.3	5.4	5.7			
Cao and Setser[27]	1985	DF–ES	3.1						
De Sousa *et al.*[16]	1985	DF–ES	2.5	4.0	4.5				
Thomas *et al.*[51]	1987	DF–LIF	2.5	4.3	4.5	4.9	4.3	3.8	4.5
Golde *et al.*[55]	1989	DF–LIF/ES	2.2	4.2	4.6	4.4			4.7
De Benedictis and Dilecce[29]	1997	DF–LIF			3.7	6.3		5.2	4.1

Dreyer *et al.*[12] also reported rate constants for $v=7$ of 7.5×10^{-12} cm^3 molecule^{-1} s^{-1}, and for $v=8$ of 5.1×10^{-12} cm^3 molecule^{-1} s^{-1}. Slanger *et al.*[36] studied the reaction over the temperature range 240–370 K, and reported $k=7.2\times10^{-12}\exp(-240/T)$ cm^3 molecule^{-1} s^{-1}. De Sousa *et al.*[16] measured the temperature dependence from 80 to 300 K for $N_2(A\,^3\Sigma_u^+, v=1,2)$, and over the range 80–560 K for $N_2(A\,^3\Sigma_u^+, v=0)$. They found that the data could be represented by an expression of the form $k=k_{300}(T/300)^{0.55}$. Over the temperature range of their measurements, the data could not be represented in Arrhenius format. The temperature dependencies are shown in Fig. 3 (data points are not shown).

This is probably the most studied of all reactions of $N_2(A\,^3\Sigma_u^+)$, and more recent values are in good agreement. The recommended value at 298 K is based on the more recent measurements as reported in Refs. 23, 13, 8, 27, 16, 51 and 55. Many of the earlier measurements are too high. The rate coefficients given in Table 7 are based on the recommended value for the room temperature rate constant and the temperature dependence for $v=0$ of De Sousa *et al.*[16] Their data are in fair agreement with those of Slanger *et al.*,[36] but cover a wider temperature range.

There have been a series of measurements of the yield of N_2O, which has declined as a function of time. Zipf[38] used a mass spectrometer to measure the yield at $m/e=44$. Although he believed that interference by CO_2 was not a problem, the reported branching ratio of 0.6 has been discounted by subsequent measurements. The most recent, by Fraser and Piper,[33] reported a branching yield of $\leq0.2\%$. Examination of the data suggests a value of $0\%\pm0.2\%$ would be equally reasonable. There is no real evidence to support the existence of this channel. This does not rule out the reaction involving $N_2(A\,^3\Sigma_u^+)$, particularly for high v, but indicates that there are other possible routes to N_2O aside from the obvious $N+NO_2$ reaction (see the discussion by Fraser *et al.*[31] of potential sources of N_2O in discharge systems).

The branching ratio for the dissociative channel to oxygen atoms is also the subject of uncertainty. Iannuzzi *et al.*[41] reported a total dissociation to O atoms of $65\%\pm10\%$ for a system of $N_2(A\,^3\Sigma_u^+, v=0,1,2)$. Reanalysis of that data by Golde and Moyle[32] led them to argue that the branching ratio increased with v, suggesting 0.57 for $v=0$ and 0.77 for $v>0$. One can surmise that for higher levels, the branching is unity. In light of the experimental difficulties in making these kinds of measurements, it is probably not too far wrong to assume a branching of unity for all levels.

However, there is one set of totally contradictory data. Fraser and Piper[33] reported the yield of O atoms to be 6.6 rather than the expected maximum of 2. They concluded that some other reactive species was present and that the yield of O atoms from the $N_2(A\,^3\Sigma_u^+)+O_2$ reaction conceivably could be zero. If that were the case, one would expect to see excess yields in other reactions for which yields have been quantitatively measured. There are data for reaction with NH_3, NO_2, and NH_2OH for which dissociative product branching is essentially unity. Until they can be confirmed, the interpretation of the data of Fraser and Piper[33] should be discounted. See also the discussion for $N_2(A\,^3\Sigma_u^+)+H$ and $N_2(A\,^3\Sigma_u^+)+NO$.

It is notable that even at the highest vibrational levels attained in any of the experiments, the rate constants were still only about 0.1 of the collision number. That implies that factors other than an energy barrier are limiting.

$N_2(A\,^3\Sigma_u^+)+O_2(^1\Delta_g)\rightarrow$ products

$N_2(A\,^3\Sigma_u^+)+O_2(^1\Delta_g)\rightarrow N_2+2O$

There are no data. Piper[17] gives an upper limit of $2\times10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ at 298 K from an analysis of possible complicating reactions involved in a study of the $N_2(A\,^3\Sigma_u^+)+O(^3P)$ reaction. This limiting value is about four times greater than that found for reaction of $N_2(A\,^3\Sigma_u^+)$ with ground state O_2. The relative slowness of the ground state reaction may be attributed to the Frank–Condon mismatch of the upper and lower states of N_2. With excited $O_2(^1\Delta_g)$, there are no energy restrictions, upper triplet O_2 states are available, and a rate constant comparable to the upper range found for vibrationally excited $N_2(A\,^3\Sigma_u^+)$ seems reasonable and is within the limit set by Piper. However, there is no direct evidence that the reaction occurs.

$N_2(A\,^3\Sigma_u^+)+O_3\rightarrow N_2+O_2+O$

$N_2(A\,^3\Sigma_u^+)+O_3\rightarrow 2NO+O$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

Source	Year	Method	0	1	2	3
Bohmer and Hack[19]	1991	DF–LIF	4.2	4.4	8.0	10.2

Bohmer and Hack[19] found that NO and O are products, and from the shape of the NO yield curve, they concluded that NO is a primary product. The major channel gives N_2+O_2+O, with a second channel (20%) leading to $2NO+O$. The branching ratio for the major channel has not been directly measured; we assume 0.8.

$N_2(A\,^3\Sigma_u^+)+NO\rightarrow N_2+NO(A\,^2\Sigma^+)$

$N_2(A\,^3\Sigma_u^+)+NO\rightarrow N_2+N+O$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

Source	Year	Method	0	1	2	3	4	5	6
Young and St. John[73]	1968	DF–ES	≈7						
Black *et al.*[7]	1969	FP–CL	8						
Young *et al.*[59]	1969	P–CL	7.0						
Callear and Wood[22]	1971	FP–CL	8.0						
Meyer *et al.*[57]	1971	DF–CL	1.4						
Dreyer and Perner[66]	1973	PR–AS	2.8	6.6					
Dreyer *et al.*[12]	1974	PR–RA	2.8	4.0	6.8	12	11	10	9.6
Mandl and Ewing[78]	1977	FP–CL	4.3						
Clark and Setser[56]	1980	DF–ES	15	15					
Piper *et al.*[20]	1986	DF–ES	6.6						
Thomas *et al.*[51]	1987	DF–LIF	5.6	7.8	8.6	10.4	9.9	12.3	11.8
De Benedictis and Dilecce[29]	1997	DF–LIF			12.2	10.8	17.3	3.0	7.4
Suzuki *et al.*[54]	1997	see text	4.8						
Shibuya *et al.*[28]	1984	LP–CL	6.9						

Dreyer *et al.*[12] also report rate constants for $v=7$ of $8.9\times10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, and for $v=8$ of $6.7\times10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$. In their experiments, Piper *et al.*[20] added CH_3F and CH_4 to relax upper vibrational levels of $N_2(A\,^3\Sigma_u^+)$, and reported little effect on the measured rate constants, implying that vibrational relaxation was not important compared to quenching. Suzuki *et al.*[54] used a pulsed discharge source, and monitored the excited state decay by measuring the current arising from collisions of the excited species on the electrode. The method is suspect; see the introductory remarks to this section. The measurements of Shibuya *et al.*[28] were independent of pressure over the range $1.3\times10^4-10^5$ Pa.

This reaction has been extensively studied, and with few exceptions, the data are in reasonable agreement. The recommended value at 298 K is the average of the more recent data from Refs. 20, 51 and 28.

The branching ratio to form NO($A\,^2\Sigma^+$) may be unity, but the data are not quantitative. Young and St. John[73] reported the rate constant for formation of NO($A\,^2\Sigma^+$) was $3\times10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, and estimated this to account for about 50% of the total reaction. Piper *et al.*[20] measured the rate constant for formation of NO($A\,^2\Sigma^+, v=0-v=2$) to be $(10\pm3)\times10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, which is significantly larger than the measured overall rate constant. They attributed the difference to possible error in the accepted lifetime of $N_2(A\,^3\Sigma_u^+)$.

Golde and Moyle[32] studied the emission from NO($A\,^2\Sigma^+$) with and without adding CF_3H to relax the higher vibrational levels of $N_2(A\,^3\Sigma_u^+)$. They argued that the total quenching rate is about the same for $v=0$ and $v=1$, but that the branching fraction to form NO($A\,^2\Sigma^+$) depends on the vibrational level of the $N_2(A\,^3\Sigma_u^+)$. They assumed a branching fraction of unity for $N_2(A\,^3\Sigma_u^+, v=0,1)$ and estimated the branching fraction for $v\geqslant2$ to be 0.78. Note that there is sufficient energy at $v=2$ to open a dissociative channel.

$N_2(A\,^3\Sigma_u^+)+N_2O\rightarrow$products

$N_2(A\,^3\Sigma_u^+)+N_2O\rightarrow2N_2+O$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

Source	Year	Method	0	1	2	3	4	5	6
Black *et al.*[7]	1969	FP-CL	10						
Young *et al.*[59]	1969	P-CL	6.4						
Callear and Wood[22]	1971	FP-CL	6.1						
Slanger *et al.*[36]	1973	FP-CL	6.4						
Clark and Setser[56]	1980	DF-ES	7.7						
Thomas *et al.*[51]	1987	DF-LIF	6.2	13	15	15	13	13	14

The data are in reasonable agreement. The recommended value at 298 K is an average of the values reported in Refs. 22, 36, and 51. Slanger *et al.*[36] measured the rate constant over the temperature range 240–370 K to be $k=9.3\times10^{-12}\exp(-120/T)\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$. The rate coefficients given in Table 7 are based on the recommended value for the rate constant at 298 K and the temperature dependence reported by Slanger *et al.*[36]

There are no quantitative product data. The mechanism probably involves energy transfer followed by dissociation.[4]

$N_2(A\,^3\Sigma_u^+)+NO_2\rightarrow N_2+NO+O$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

Source	Year	Method	0	1	2	3
Bohmer and Hack[21]	1990	DF–LIF	1.3	1.4	3.0	3.0

Bohmer and Hack[21] reported detecting NO and O as products, giving the branching ratio for formation of NO to be 1 ± 0.2.

$N_2(A\,^3\Sigma_u^+)+N\rightarrow N_2+N$

$N_2(A\,^3\Sigma_u^+)+N\rightarrow N_2+N(^2P)$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

Source	Year	Method	0	1
Young and St. John[88]	1968	DF-ES	5.0	6.5
Meyer *et al.*[58]	1970	DF-ES	5.2	5.2
Piper[87]	1989	DF-ES	4.0	4.0
Dunn and Young[76]	1976	PD-ES	4.8	4.8
Vadaud *et al.*[26]	1976	see text	3.5	

Meyer *et al.*[58] measured the rate constant relative to the rate constant for the $N_2(A\,^3\Sigma_u^+)+O_2$ reaction. They used $k(O_2)=6\times10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, considerably lower than the value recommended here of $k(O_2)=2.5\times10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$. These data are discounted.

Vadaud *et al.*,[26] used a discharge flow system combined

TABLE 8. Recommended values for the rate constants of the reactions of $N_2(A\,^3\Sigma_u^+)$ with species containing C[a]

Reaction	A	E/R	$k(298)$	$f(298)$[b]	Notes
$N_2(A\,^3\Sigma_u^+)+CH_4\rightarrow$products	1.2×10^{-10}	3170	3×10^{-15}	2	300–360 K
$N_2(A\,^3\Sigma_u^+)+CH_3F\rightarrow$products			$\leqslant10^{-14}$		
$N_2(A\,^3\Sigma_u^+)+CH_3Cl\rightarrow$products			8.0×10^{-12}	2	
$N_2(A\,^3\Sigma_u^+)+CH_3Br\rightarrow$products			1.8×10^{-10}	2	
$N_2(A\,^3\Sigma_u^+)+CH_3I\rightarrow$products			4.3×10^{-10}	2	
$N_2(A\,^3\Sigma_u^+)+CHF_2Cl\rightarrow$products			1.0×10^{-13}	2	
$N_2(A\,^3\Sigma_u^+)+CHF_3\rightarrow$products			$\leqslant10^{-14}$		
$N_2(A\,^3\Sigma_u^+)+CF_2Cl_2\rightarrow$products			1.5×10^{-13}	2	
$N_2(A\,^3\Sigma_u^+)+CF_3Cl\rightarrow$products			6.0×10^{-14}	2	
$N_2(A\,^3\Sigma_u^+)+CF_3I\rightarrow$products			2.0×10^{-10}	2	
$N_2(A\,^3\Sigma_u^+)+CF_4\rightarrow$products			$\leqslant10^{-14}$		
$N_2(A\,^3\Sigma_u^+)+C_2H_6\rightarrow$products	1.8×10^{-10}	1980	2.3×10^{-13}	2	300–370 K
$N_2(A\,^3\Sigma_u^+)+CH_2FCF_3\rightarrow$products					see text
$N_2(A\,^3\Sigma_u^+)+C_2F_6\rightarrow$products			$\leqslant10^{-14}$		
$N_2(A\,^3\Sigma_u^+)+C_3H_8\rightarrow$products			1.3×10^{-12}	2	
$N_2(A\,^3\Sigma_u^+)+$cy-$C_3H_6\rightarrow$products			$\leqslant2\times10^{-14}$		
$N_2(A\,^3\Sigma_u^+)+n$-$C_4H_{10}\rightarrow$products			2.7×10^{-12}	2	
$N_2(A\,^3\Sigma_u^+)+C_2H_4\rightarrow$products			1.1×10^{-10}	1.2	
$N_2(A\,^3\Sigma_u^+)+C_3H_6\rightarrow$products			2.8×10^{-10}	2	
$N_2(A\,^3\Sigma_u^+)+cis$-$C_4H_8\rightarrow$products			2.2×10^{-10}	2	
$N_2(A\,^3\Sigma_u^+)+CH_2CCH_2\rightarrow$products			3.7×10^{-10}	2	
$N_2(A\,^3\Sigma_u^+)+CH_2CHCHCH_2\rightarrow$products			3.5×10^{-10}	2	
$N_2(A\,^3\Sigma_u^+)+C_2H_2\rightarrow$products			2.0×10^{-10}	1.3	
$N_2(A\,^3\Sigma_u^+)+CH_3CCH\rightarrow$products			2.8×10^{-10}	2	
$N_2(A\,^3\Sigma_u^+)+C_6H_6$(benzene)$\rightarrow$products			1.6×10^{-10}	2	
$N_2(A\,^3\Sigma_u^+)+C_2N_2\rightarrow$products			4.0×10^{-11}	1.3	
$N_2(A\,^3\Sigma_u^+)+HCN\rightarrow$products			6×10^{-12}	2	
$N_2(A\,^3\Sigma_u^+)+CH_3CN\rightarrow$products			1.3×10^{-11}	1.3	
$N_2(A\,^3\Sigma_u^+)+CO\rightarrow$products	3.8×10^{-11}	940	1.6×10^{-12}	1.3	260–360 K
$N_2(A\,^3\Sigma_u^+)+CO_2\rightarrow$products			2×10^{-14}	2	
$N_2(A\,^3\Sigma_u^+)+CH_2CO\rightarrow$products			6.5×10^{-14}	2	
$N_2(A\,^3\Sigma_u^+)+CH_3OH\rightarrow$products			4.3×10^{-12}	2	
$N_2(A\,^3\Sigma_u^+)+(CH_3)_2O\rightarrow$products			7.5×10^{-12}	2	
$N_2(A\,^3\Sigma_u^+)+(CH_3)_2CO\rightarrow$products			1.1×10^{-10}	2	
$N_2(A\,^3\Sigma_u^+)+CH_3SH\rightarrow$products			4.3×10^{-10}	2	

[a] Preexponential factors, A, and rate constants, $k(298)$, in units of $cm^3\,molecule^{-1}\,s^{-1}$; E/R in units of K.

[b] Multiplicative error factor. Applies to 298 K values only. Error limits are larger at lower or higher temperatures.

with mass spectrometry and isothermal calorimetry, to follow the reaction. However, the method is not necessarily specific to detection of $N_2(A\,^3\Sigma_u^+)$. Piper[87] notes that the reported wall quenching rate for $N_2(A\,^3\Sigma_u^+)$ of $1.8\times10^{-5}\,s^{-1}$ is much lower than that found by other workers ($\approx1\,s^{-1}$). These results are also discounted.

The recommended value for the rate constant at 298 K is an average of the values reported by Piper[87] and Dunn and Young.[76]

Meyer *et al.*[58] observed emission from $N(^2P)$ which they found to be directly proportional to the $N_2(A\,^3\Sigma_u^+)$ and to the $N(^4S)$ concentrations. They did not observe $N(^2D)$.

Piper[87] measured the rate constants for total quenching of $N_2(A\,^3\Sigma_u^+)$ and the rate constants for formation (excitation) of $N(^2P)$. The measured rate constant for excitation of $N(^2P)$ by $N_2(A\,^3\Sigma_u^+, v=0)$ was $19\times10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$, and for excitation of $N(^2P)$ by $N_2(A\,^3\Sigma_u^+, v=1)$ was $5\times10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$. Although the authors give several possible reasons for the great discrepancy between their values (for $v=0$) and the reported overall quenching rate constants, the data are little more than suggestive that the excitation channel is the major path. It should be noted that one possible explanation offered by Piper[87] for the difference in rate constants is that some as yet unidentified additional metastable N_2 molecule is produced in the discharge. Excess product yields were reported from the same laboratory in the case of the $N_2(A\,^3\Sigma_u^+)+O_2$ reaction (Fraser and Piper[33]).

$N_2(A\,^3\Sigma_u^+)+N_2 \rightarrow N_2+N_2$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of 10^{-18} cm^3 molecule^{-1} s^{-1}.

Source	Year	Method	0	1
Callear and Wood[22]	1971	FP–CL	≤ 10	
Dreyer and Perner[66]	1973	PR–RA	≤ 370	≤ 340
Vadaud *et al.*[26]	1976	see text	45	
Levron and Phelps[25]	1978	PD–ES	2.6	38
Suzuki *et al.*[64]	1993	see text	37	
Suzuki *et al.*[54]	1997	see text	1.8	

Measurement of the rate constants of very slow reactions is extremely difficult, but in the case of this reaction the rate constant is a necessary input to models of air discharges. It is therefore particularly unfortunate that the measurements are in such disagreement. The unexplained disagreement in measurements from the same laboratory in the case of Suzuki *et al.*[54,64] casts great uncertainty on the validity of their experimental approach. They used a pulsed discharge source, and monitored the excited state decay by measuring the current arising from collisions of the excited species on the electrode. The method is suspect; see the introductory remarks to this section. In the experiments of Dreyer and Perner,[66] even though the total pressure was high ($>10^5$ Pa), the $N(^4S)$ concentration was also very high, so that quenching by $N(^4S)$ could have been important. Therefore, the rate constants are upper limits only. Vidaud *et al.*,[26] used a discharge flow system combined with mass spectrometry and isothermal calorimetry. However, the experiment is not necessarily specific to detection of $N_2(A\,^3\Sigma_u^+)$.

Levron and Phelps[25] reported their measurement as an upper limit to allow for possible impurities in their nitrogen supply. Their value is the basis for the recommended upper limit.

$N_2(A\,^3\Sigma_u^+)+N_2(A\,^3\Sigma_u^+) \rightarrow$ products
$N_2(A\,^3\Sigma_u^+)+N_2(A\,^3\Sigma_u^+) \rightarrow N_2+N_2(B\,^3\Pi_g)$
$N_2(A\,^3\Sigma_u^+)+N_2(A\,^3\Sigma_u^+) \rightarrow N_2+N_2(C\,^3\Pi_u)$

These energy pooling reactions are extremely complex; there are channels leading to $N_2(B\,^3\Pi_g)$, $N_2(C\,^3\Pi_u)$, and other unidentified states including that responsible for the Herman infrared system (HIR). For the overall reaction, Piper[24] suggests $k=(3-4)\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which is the basis of the recommended value. For detailed discussions of the excited state system see Refs. 24 and 26–28.

$N_2(A\,^3\Sigma_u^+)+CH_4 \rightarrow$ products

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of 10^{-13} cm^3 molecule^{-1} s^{-1}.

Source	Year	Method	0	1	2	3	4	5	6
Black *et al.*[17]	1969	FP–CL	0.03						
Young *et al.*[59]	1969	P–CL	≤ 0.07						
Meyer *et al.*[57]	1971	DF–CL	≤ 0.2						
Callear and Wood[22]	1971	FP–CL	≤ 0.017						
Slanger *et al.*[36]	1973	FP–CL	0.032						
Clark and Setser[56]	1980	DF–ES	≤ 0.1	11					
Thomas *et al.*[6]	1983	DF–LIF		15	31	50			
Piper *et al.*[77]	1985	DF–ES		14					
Golde *et al.*[55]	1989	DF–LIF		12	23	29	40	40	51

Slanger *et al.*[36] studied the reaction over the temperature range 300–360 K and reported $k=1.3\times 10^{-10} \times \exp(-3170/T)$ cm^3 molecule^{-1} s^{-1}. These data are the basis for the recommended value. However, it must be noted that their experimental method is not sensitive to the vibrational level, but rather refers to some mix of vibrational levels. Examination of the whole body of their data indicates that this has not led to erroneous results. For this reaction the ratio of rate constants $v=1/v=0$ is about 100, and the possibility for error is much greater.

Golde *et al.*[55] detected H atoms as a product, but were not able to make a quantitative measurement. By studying the reaction with added CF_3H to relax the upper vibrational levels of $N_2(A\,^3\Sigma_u^+)$, they deduced that vibrational relaxation was the principal deactivation process for $v>0$, in agreement with Thomas *et al.*,[6] with maybe 12% going by electronic quenching. In the absence of product data, it is not clear how much, if any, of the vibrational energy is available to surmount the energy barrier.

$N_2(A\,^3\Sigma_u^+)+CH_3F\rightarrow$products

The only measurements are by Clark and Setser,[56] using the discharge flow–emission spectroscopy technique. They reported for $N_2(A\,^3\Sigma_u^+, v=0)$, $k\leq 10^{-14}$ cm³ molecule⁻¹ s⁻¹.

$N_2(A\,^3\Sigma_u^+)+CH_3Cl\rightarrow$products

The only measurements are by Clark and Setser,[56] using the discharge flow–emission spectroscopy technique. They reported for $N_2(A\,^3\Sigma_u^+, v=0)$, $k=8.0\times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Callear and Wood[22] detected excited iodine atoms as a product, but did not observe CH_3 in absorption.

$N_2(A\,^3\Sigma_u^+)+CH_3Br\rightarrow$products

The only measurements are by Clark and Setser,[56] using the discharge flow–emission spectroscopy technique. They reported for $N_2(A\,^3\Sigma_u^+, v=0)$, $k=1.8\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

$N_2(A\,^3\Sigma_u^+)+CH_3I\rightarrow$products

The only measurements are by Clark and Setser,[56] using the discharge flow–emission spectroscopy technique. They reported for $N_2(A\,^3\Sigma_u^+, v=0)$, $k=4.3\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

$N_2(A\,^3\Sigma_u^+)+CHF_2Cl\rightarrow$products

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of 10^{-12} cm^3 molecule^{-1} s^{-1}.

Source	Year	Method	0	1	2	3	4	5	6
Golde *et al.*[55]	1989	DF-LIF	0.1	1.2	3.7	12	18	22	30

Golde *et al.*[55] suggest $N_2(A\,^3\Sigma_u^+)+CF_2HCl\rightarrow N_2+CF_2H+Cl$, as the major channel.

$N_2(A\,^3\Sigma_u^+)+CHF_3\rightarrow$products

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of 10^{-12} cm^3 molecule^{-1} s^{-1}.

Source	Year	Method	0	1	2	3
Piper *et al.*[77]	1985	DF–ES		0.9		
Tao *et al.*[63]	1992	DF–LIF	≤0.01	1.0	2.6	2.9

Piper *et al.*[77] identified the process as $N_2(A\,^3\Sigma_u^+, v=1)+CHF_3\rightarrow N_2(A\,^3\Sigma_u^+, v=0)+CHF_3$. Tao *et al.*[63] also reported the dominant process to be vibrational relaxation.

$N_2(A\,^3\Sigma_u^+)+CF_2Cl_2\rightarrow$products

There are two sets of measurements. Cao and Setser[84] used discharge flow with emission spectroscopy or chemiluminescence detection and reported rate constants for $v=0$ of 1.5×10^{-13} cm^3 molecule^{-1} s^{-1} and for $v=1$ of 12×10^{-13} cm^3 molecule^{-1} s^{-1}. Suzuki *et al.*[54] used a pulsed discharge source, and monitored the excited state decay by measuring the current arising from collisions of the excited species on the electrode. The method is suspect; see the introductory remarks to this section. They reported $k=8.3\times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for some undetermined mix of vibrational levels, possibly $v=0$, 1, and 2.

The recommended value is from Cao and Setser.[82]

Golde[4] suggests simple bond cleavage as the dominant mechanism, possibly $N_2(A\,^3\Sigma_u^+)+CF_2Cl_2\rightarrow N_2+CF_2Cl+Cl$.

$N_2(A\,^3\Sigma_u^+)+CF_3Cl\rightarrow$products

$N_2(A\,^3\Sigma_u^+)+CF_3Cl\rightarrow N_2+CF_3+Cl$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of 10^{-12} cm^3 molecule^{-1} s^{-1}.

Source	Year	Method	0	1	2	3	4	5	6
Golde *et al.*[55]	1989	DF-LIF	0.06	0.29	1.3	5.0	9.1	11	17

Golde *et al.*[55] concluded that the main electronic quenching channel produced CF_3+Cl.

$N_2(A\,^3\Sigma_u^+)+CF_3I \rightarrow$ products

The only measurements are by Piper *et al.*[77] using discharge flow with emission spectroscopy. They reported for $N_2(A\,^3\Sigma_u^+, v=0)$, $k=2.0\times10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$, and for $N_2(A\,^3\Sigma_u^+, v=1)$, $k=2.1\times10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$. The major quenching channel is probably decomposition to CF_3+I.

$N_2(A\,^3\Sigma_u^+)+CF_4 \rightarrow$ products

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$.

Source	Year	Method	0	1	2	3	4	5	6
Thomas *et al.*[6]	1983	DF–LIF		0.47	1.8	5.5			
Piper *et al.*[77]	1985	DF–ES	≤0.01	0.3					
Golde *et al.*[55]	1989	DF–LIF		0.28	1.2	3.4	6.2	13	22

Vibrational relaxation is probably the dominant channel.

$N_2(A\,^3\Sigma_u^+)+C_2H_6 \rightarrow$ products

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-13}\,cm^3\,molecule^{-1}\,s^{-1}$.

Source	Year	Method	0	1	2	3	4	5	6
Young *et al.*[59]	1969	P-CL	≤0.05						
Callear and Wood[22]	1971	FP-CL	3.6						
Meyer *et al.*[57]	1971	DF-CL	≤0.2						
Dreyer and Perner[66]	1973	PR-AS	2.9	36	74	111	170	160	210
Slanger *et al.*[36]	1973	FP-CL	2.2						
Clark and Setser[56]	1980	DF-ES		72					

Slanger *et al.*[36] studied the reaction over the temperature range 300–370 K and reported $k=1.6\times10^{-10}\times\exp(-1980/T)\,cm^3\,molecule^{-1}\,s^{-1}$. This value, adjusted slightly upwards, is the basis for the recommended value. But see the comments under the CH_4 reaction.

The reaction is probably mostly vibrational relaxation for $v\geqslant2$,[66] with some contribution by electronic quenching to dissociative products.

$N_2(A\,^3\Sigma_u^+)+CH_2FCF_3 \rightarrow$ products

The only measurements are by Suzuki *et al.*[54] who used a technique in which excited molecules were formed in a dc discharge, and the excited state population monitored by following the current generated after the end of the discharge, which was attributed to the electrons released when the excited species collided with the electrode. They reported $k=2.96\times10^{-15}\,cm^3\,molecule^{-1}\,s^{-1}$ for some undetermined mix of vibrational levels, probably $v=0$, 1, and 2. Since there is no way to characterize the species responsible for the electron release, these data are suspect (see the introduction to this section).

$N_2(A\,^3\Sigma_u^+)+C_2F_6 \rightarrow$ products

The only measurements are by Clark and Setser,[56] using the discharge flow–emission spectroscopy technique. They reported for $N_2(A\,^3\Sigma_u^+, v=0)$, $k=\leqslant0.1\times10^{-13}\,cm^3\,molecule^{-1}\,s^{-1}$, and for $N_2(A\,^3\Sigma_u^+, v=1)$, $k=2.9\times10^{-13}\,cm^3\,molecule^{-1}\,s^{-1}$.

Vibrational relaxation is the dominant channel.

$N_2(A\,^3\Sigma_u^+)+C_3H_8 \rightarrow$ products

The only measurements are by Callear and Wood,[22] using the flash photolysis–emission spectroscopy technique. They reported $k=1.3\times10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$.

$N_2(A\,^3\Sigma_u^+)+cy\text{-}C_3H_6 \rightarrow$ products

The only measurements are by Meyer *et al.*,[57] using the discharge flow–chemiluminescence technique. They reported $k = \leq 2\times10^{-14}$ cm^3 molecule^{-1} s^{-1}.

$N_2(A\,^3\Sigma_u^+)$+n-C_4H_{10}→products

The only measurements are by Callear and Wood,[22] using the flash photolysis–emission spectroscopy technique. They reported $k=2.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.

$N_2(A\,^3\Sigma_u^+)+C_2H_4$→products

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of 10^{-10} cm^3 molecule^{-1} s^{-1}.

Source	Year	Method	0	1	2	3	4	5	6
Black *et al.*[7]	1969	FP–CL	1.2						
Young *et al.*[59]	1969	P–CL	1.5						
Meyer *et al.*[57]	1971	DF–CL	1.6						
Callear and Wood[22]	1971	FP–CL	1.1						
Clark and Setser[56]	1980	DF–ES	1.2	1.4					
Dreyer *et al.*[66]	1973	PR–AS	0.64	1.08	1.09	1.11	1.19	1.09	1.45
Cao and Setser[27]	1985	DF–CL	1.2						
Thomas *et al.*[51]	1987	DF–LIF	1.0	1.1	0.89	1.0	0.92	0.95	1.2
Ho and Golde[61]	1991	DF–ES	1.2						

The results are in good agreement. An average value based on the data of Refs. 22, 27, 51 and 61 is the basis for the recommended value at 298 K.

Meyer *et al.*[57] collected the condensable reaction products and identified C_2H_2 as a product. They proposed a mechanism: $N_2(A\,^3\Sigma_u^+)+C_2H_4 \rightarrow N_2+(C_2H_4)^* \rightarrow H_2+C_2H_2$. There was no evidence for products arising from cleavage of C–H bonds. Quantitative product yields were not reported. Golde[4] also argued that dissociative channels are minor, with the branching fraction to yield H atoms being about 0.2. However, at higher vibrational levels, one can expect branching ratios to change and total yields to increase.

$N_2(A\,^3\Sigma_u^+)+C_3H_6$→products

The only measurements are by Meyer *et al.*,[57] using the discharge flow–chemiluminescence technique. They reported $k=2.8\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.

$N_2(A\,^3\Sigma_u^+)$+*cis*-2-C_4H_8→products

The only measurements are by Meyer *et al.*,[57] using the discharge flow–chemiluminescence technique. They reported $k=2.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1}. These workers also collected the condensable reaction products, and found *trans*-2-C_4H_8 and 1,3-butadienne as major products. They proposed a mechanism: $N_2(A\,^3\Sigma_u^+)+cis\text{-}2\text{-}C_4H_8 \rightarrow N_2+(C_4H_8)^* \rightarrow trans\text{-}2\text{-}C_4H_8$ or $H+C_4H_7$. Quantitative product yields were not reported.

$N_2(A\,^3\Sigma_u^+)+CH_2CCH_2$→products

The only measurements are by Bohmer and Hack,[34] using the discharge flow–laser induced fluorescence technique. They reported for $N_2(A\,^3\Sigma_u^+, v=0-3)$, $k=3.7\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of vibrational level. Possible decomposition products include CH_2 and C_2H_2, but there are no data.

$N_2(A\,^3\Sigma_u^+)+CH_2CHCHCH_2$→products

The only measurements are by Meyer *et al.*,[57] using the discharge flow–chemiluminescence technique. They reported $k=3.5\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.

$N_2(A\,^3\Sigma_u^+)+C_2H_2$→products

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of 10^{-10} cm^3 molecule^{-1} s^{-1}.

Source	Year	Method	0	1	2	3
Young *et al.*[59]	1969	P–CL	1.2			
Callear and Wood[22]	1971	FP–CL	1.6			
Meyer *et al.*[57]	1971	DF–CL	2.5			
Bohmer and Heck[34]	1991	DF–LIF	2.0	2.0	2.0	2.0

The data are in reasonable agreement. The recommended value is from Bohmer and Hack.[34]

There are no product data, but the high rate constant and lack of dependence on the vibrational level suggest a dissociative quenching mechanism.

$N_2(A\,^3\Sigma_u^+)+CH_3CCH\rightarrow$products

The only measurements are by Bohmer and Hack,[34] using the discharge flow–laser induced fluorescence technique. They reported for $N_2(A\,^3\Sigma_u^+, v=0-3)$, $k=2.8\times10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$, independent of vibrational level. They suggest as possible products C_2H_2 and CH_2. There are no product data.

$N_2(A\,^3\Sigma_u^+)+C_6H_6$ (benzene)$\rightarrow$products

The only measurements are by Meyer *et al.*,[57] using the discharge flow–chemiluminescence technique. They reported $k=1.6\times10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$. There are no product data.

$N_2(A\,^3\Sigma_u^+)+C_2N_2\rightarrow$products
$N_2(A\,^3\Sigma_u^+)+C_2N_2\rightarrow2CN(X\,^2\Sigma^+)+N_2$

The rate constant data for the overall reaction are summarized in the following table for $N_2(A\,^3\Sigma_u^+, v=0)$. Rate constants in units of $10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$.

Source	Year	Method	0
Young *et al.*[59]	1969	P–CL	4.2
Meyer *et al.*[57]	1971	DF–CL	5.7
Clark and Setser[56]	1980	DF–ES	4.0

The data are in good agreement. The recommended value at 298 K is based on the data of Clark and Setser.[56]

Meyer *et al.*[74] studied the emission spectrum arising from the formation of $C_2N_2(a\,^3\Sigma_u^+)$. They also observed the formation of excited CN radicals, presumably arising from excitation of CN radical formed in the $N_2(A\,^3\Sigma_u^+)+C_2N_2$ reaction. Although there are no quantitative data on product yields, they suggested the reaction $N_2(A\,^3\Sigma_u^+)+C_2N_2\rightarrow2CN(X\,^2\Sigma^+)+N_2$.

$N_2(A\,^3\Sigma_u^+)+HCN\rightarrow$products
$N_2(A\,^3\Sigma_u^+)+HCN\rightarrow H+CN+N_2$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$.

Source	Year	Method	0	1	2	3
Clark and Setser[56]	1980	DF–ES	12			
Tao *et al.*[63]	1992	DF–LIF	0.58	1.9	2.9	3.1

The very large disagreement between the values for $v=0$ is inexplicable, since the same workers are in good agreement for rate measurements for CH_3CN (see below). Tao *et al.*[63] repeated their rate measurement for $v=0$ using emission spectroscopy, finding $k=0.63\times10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ in agreement with their LIF result. Their data are accepted.

Product yields were measured by Tao *et al.*[63] For $v=0$, the H atom yield was 70%. For the vibrationally unrelaxed system consisting of vibrational levels up to at least 4, the yield was 81%. The balance is presumably due to a second quenching channel, which they suggest might lead to an excited triplet state of HCN.

$N_2(A\,^3\Sigma_u^+)+CH_3CN\rightarrow$products
$N_2(A\,^3\Sigma_u^+)+CH_3CN\rightarrow CH_3+CN+N_2$
$N_2(A\,^3\Sigma_u^+)+CH_3CN\rightarrow H+CH_2CN+N_2$

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$.

Source	Year	Method	0	1	2	3	4
Clark and Setser[56]	1980	DF–ES	1.9				
Tao *et al.*[63]	1992	DF–LIF	1.3	3.2	5.8	6.7	6.0

The data are in good agreement. The recommended value at 298 K is based on the data of Tao *et al.*[63]

Product yields were measured by Tao *et al.*[63] For $v=0$, the H atom yield was 70%, while for the vibrationally unrelaxed system consisting of vibrational levels up to at least 4, the yield was 62%. This suggests that other channels including CH_3+CN are competitive. Thus, the yield of CN increased from 8% at $v=0$ to an average of 59% at $v\geq3$. As in the case of the HCN reaction, the dissociative channels only account for about 80% of the total reaction. The balance is presumably due to a second quenching channel, which they suggest might lead to formation of an excited triplet state of CH_3CN.

$N_2(A\,^3\Sigma_u^+)+CO\rightarrow$products

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of $10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$.

Source	Year	Method	0	1	2	3	4	5	6
Black *et al.*[7]	1969	FP–CL	2.5						
Young *et al.*[59]	1969	P–CL	1.9						
Callear and Wood[22]	1971	FP–CL	1.5	24					
Meyer *et al.*[57]	1971	DF–CL		22					

Slanger *et al.*[36]	1973	FP–CL	1.7						
Dreyer *et al.*[12]	1974	PR–AS	1.8	18	46	21	19	16	17
Clark and Setser[56]	1980	DF–ES	5	25					
Thomas *et al.*[51]	1987	DF–LIF	1.5	17	49	18	19	10	14
Suzuki *et al.*[64]	1993	see text	0.6						

Dreyer *et al.*[12] also reported for $v=7$, $k=9.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, and for $v=8$, $k=7.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. Slanger *et al.*[36] studied the reaction over the temperature range 260–360 K, and reported $k=3.9\times10^{-11}\exp(-940/T)$ cm^3 molecule^{-1} s^{-1}. Suzuki *et al.*[64] used a pulsed discharge source, and monitored the excited state decay by measuring the current arising from collisions of the excited species on the electrode. The method is suspect (see the introductory remarks to this section).

The data of Refs. 7, 59, 56, and 64 are discounted (see the introduction to this section). The recommended value at 298 K is based on the average of the remaining values. The recommended rate coefficients are based on the recommended value at 298 K and the temperature dependence reported by Slanger *et al.*[36]

The sharp increase in rate constant going from $v=0$ to $v=3$ followed by a sudden drop-off is discussed by Thomas *et al.*[51] in terms of the energy resonance between the $N_2(A\,^3\Sigma_u^+)$ and CO (X) states. The rate constants at high vibrational levels $[(1-2)\times10^{-11}$ cm^3 molecule^{-1} s$^{-1}]$ are significantly below the collision number. The reported A factor is not too different from the measured maximum rate constant (at $v=2$). The temperature dependence is readily interpreted in terms of a $T^{0.5}$ factor implying a zero activation energy.

$N_2(A\,^3\Sigma_u^+)+CO_2\rightarrow$products

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of 10^{-13} cm^3 molecule^{-1} s^{-1}.

Source	Year	Method	0	1	2	3	4	5	6
Black *et al.*[7]	1969	FP–CL	0.5						
Young *et al.*[59]	1969	P–CL	≤0.2						
Callear and Wood[22]	1971	FP–CL	≤0.013						
Meyer *et al.*[57]	1971	DF–CL	≤0.2						
Dreyer *et al.*[12]	1974	PR–AS	0.099	0.2	1.5	2.9	4.9	16	31

Dreyer *et al.*[12] also reported for $v=7$, $k=48\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, and for $v=8$, $k=47\times10^{-13}$ cm^3 molecule^{-1} s^{-1}. The recommended value is based on their data (for $v=0$), adjusted upwards by a factor of 2 (see the introduction to this section).

$N_2(A\,^3\Sigma_u^+)+CH_3OH\rightarrow$products
$N_2(A\,^3\Sigma_u^+)+CH_3OH\rightarrow CH_3O+H+N_2$

The only measurements are by Clark and Setser,[56] using the discharge flow–emission spectroscopy technique. They reported for $N_2(A\,^3\Sigma_u^+, v=0)$, $k=4.3\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Tao *et al.*[65] found that H atoms are the primary product with a branching yield of 0.86 (relative to an assumed branching yield of 1.0 for the corresponding reaction of NH_3). Studies of reactions of labeled CH_3OH indicate that the reaction involved scission of the O–H bond rather than the C–H bond. The yield of OH was very small. As in other reactions of $N_2(A\,^3\Sigma_u^+)$ the products do not necessarily correspond to the lowest energy path. In other experiments, Golde and Moyle[32] from a study of the $N_2(A,v-X)$ emission found that $N_2(A\,^3\Sigma_u^+, v=1)$ is removed at about twice the rate as $N_2(A\,^3\Sigma_u^+, v=0)$. From a study of the H atom yields with or without added CF_3H which relaxes the upper vibrational levels of $N_2(A\,^3\Sigma_u^+)$, they concluded that dissociative electronic quenching increased significantly with vibrational level, and that vibrational relaxation was a minor process.

$N_2(A\,^3\Sigma_u^+)+CH_2CO\rightarrow$products

The rate constant data for the overall reaction are summarized in the following table as a function of the vibrational level of $N_2(A\,^3\Sigma_u^+)$. Rate constants in units of 10^{-14} cm^3 molecule^{-1} s^{-1}.

Source	Year	Method	0	1	2	3
Bohmer and Hack[15]	1989	DF–LIF	6.5	9.5	14.5	16

TABLE 9. Recommended values for the rate constants of the reactions of $N_2(A\,^3\Sigma_u^+)$ with miscellaneous species[a]

Reaction	$k(298)$, $v=0$	$k(298)$, $v=1$	$f(298)$[b]	Method references notes	Year
$N_2(A\,^3\Sigma_u^+)+HCl\rightarrow$products	1.3×10^{-12}		2	DF-ES[56] [c]	1980
$N_2(A\,^3\Sigma_u^+)+HBr\rightarrow$products	7.8×10^{-11}		2	DF-ES[56]	1980
$N_2(A\,^3\Sigma_u^+)+HI\rightarrow$products	2.8×10^{-10}		2	DF-ES[56]	1980
$N_2(A\,^3\Sigma_u^+)+H_2S\rightarrow$products	3.0×10^{-10}		2	DF-ES[56]	1980
$N_2(A\,^3\Sigma_u^+)+F_2\rightarrow$products	2.0×10^{-13}	1.5×10^{-12}	2	DF-RF[15] [d]	1989
$N_2(A\,^3\Sigma_u^+)+Cl_2\rightarrow$products	7.8×10^{-11}		2	DF-ES/CL[27]	1985
$N_2(A\,^3\Sigma_u^+)+Br_2\rightarrow$products	1.2×10^{-10}		2	DF-ES/CL[27]	1985
$N_2(A\,^3\Sigma_u^+)+I_2\rightarrow$products	6.9×10^{-12}			FP-CL[78]	1977
	2.3×10^{-10}			DF-ES/CL[27]	1985
	2.3×10^{-10}		2	Recommended[e]	
$N_2(A\,^3\Sigma_u^+)+IF\rightarrow$products	1.9×10^{-10}	2.0×10^{-10}	2	DF-ES[77]	1985
$N_2(A\,^3\Sigma_u^+)+ICl\rightarrow$products	8.0×10^{-11}		2	DF-ES/CL[27]	1985
$N_2(A\,^3\Sigma_u^+)+IBr\rightarrow$products	1.5×10^{-10}		2	DF-ES/CL[82]	1988
$N_2(A\,^3\Sigma_u^+)+NF_3\rightarrow$products	3×10^{-13}			DF-ES[77]	1985
	1×10^{-13}			DF-ES/CL[82]	1988
	2×10^{-13}		2	Recommended	
$N_2(A\,^3\Sigma_u^+)+SF_6\rightarrow$products		1×10^{-14}	2	DF-ES[77]	1985
$N_2(A\,^3\Sigma_u^+)+SO\rightarrow$products	1.2×10^{-10}			DF-ES/CL[27]	1985
	1.1×10^{-10}			DF-ES/CL[82]	1988
	1.1×10^{-10}		2	Recommended	
$N_2(A\,^3\Sigma_u^+)+SO_2\rightarrow$products	4.8×10^{-11}			DF-ES[57]	1971
	3.0×10^{-11}			DF-ES[56]	1980
	2.8×10^{-11}			DF-ES/CL[27]	1985
	3.5×10^{-11}		2	Recommended	
$N_2(A\,^3\Sigma_u^+)+SOCl_2\rightarrow$products	8.7×10^{-11}			DF-ES/CL[27]	1985
	9.4×10^{-11}			DF-ES/CL[82]	1988
	7.0×10^{-11}		2	Recommended	
$N_2(A\,^3\Sigma_u^+)+SOF_2\rightarrow$products	7×10^{-12}		2	DF-ES/CL[82]	1988
$N_2(A\,^3\Sigma_u^+)+SO_2F_2\rightarrow$products	1.5×10^{-13}		2	DF-ES/CL[82]	1988
$N_2(A\,^3\Sigma_u^+)+S_2\rightarrow$products	6.0×10^{-11}		2	DF-ES/CL[27]	1985
$N_2(A\,^3\Sigma_u^+)+S_2Cl_2\rightarrow$products	6.0×10^{-11}		2	DF-ES/CL[27]	1985
$N_2(A\,^3\Sigma_u^+)+PF_3\rightarrow$products	1.5×10^{-11}		2	DF-ES/CL[82]	1988
$N_2(A\,^3\Sigma_u^+)+PCl_3\rightarrow$products	5.0×10^{-11}		2	DF-ES/CL[82]	1988
$N_2(A\,^3\Sigma_u^+)+PF_5\rightarrow$products	5×10^{-13}		2	DF-ES/CL[82]	1988
$N_2(A\,^3\Sigma_u^+)+POCl_3\rightarrow$products	3×10^{-12}		2	DF-ES/CL[82]	1988

[a] Preexponential factors, A, and rate constants, $k(298)$, in units of $cm^3\,molecule^{-1}\,s^{-1}$; E/R in units of K.

[b] Multiplicative error factor. Applies to 298 K values only. Error limits are larger at lower or higher temperatures.

[c] Golde,[88] quoting unpublished data of Golde, Ho, and Tao, indicated that the yield of Cl atoms was about unity and increased going from $v=0$ to $v\geqslant1$.

[d] Bohmer and Hack[15] also reported for $v=2$, $k=1.5\times10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$, and for $v=3$, $k=1.7\times10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$. There was no evidence for vibrational relaxation of the higher states.

[e] The two sets of reported data are in serious disagreement. Mandl and Ewing,[78] also obtained the rate constant for the NO reaction from the intercept of their plot of the reciprocal of the decay time as a function of the I_2 concentration, finding a value close to the accepted one. Similarly, Cao and Setser,[27] measured rate constants for the reaction with O_2 and C_2H_4, and also reported values in reasonable agreement with the accepted ones. The problem is thus due to a source of systematic error in one or both experiments. One possibility is the determination of the concentration of I_2. Mandl and Ewing used a static temperature controlled iodine source. However, it would require an enormous error in assigning the effective vapor pressure to account for the discrepancy (an error of 5 K leads to an error of 2 in concentration). Cao and Setser gave no experimental detail. Since all measured rate constants for the dihalogens, with the exception of F_2, cluster around $10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$, the data of Cao and Setser[27] are accepted.

There are no product data; possible products are CH_2+CO+N_2.

$N_2(A\,^3\Sigma_u^+)+(CH_3)_2O \rightarrow$ products

The only measurements are by Clark and Setser,[56] using the discharge flow–emission spectroscopy technique. They reported for $N_2(A\,^3\Sigma_u^+, v=0)$, $k=7.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.

$N_2(A\,^3\Sigma_u^+)+(CH_3)_2CO \rightarrow$ products

The only measurements are by Clark and Setser,[56] using the discharge flow–emission spectroscopy technique. They reported for $N_2(A\,^3\Sigma_u^+, v=0)$, $k=1.1\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.

$N_2(A\,^3\Sigma_u^+)+CH_3SH \rightarrow$ products

The only measurements are by Clark and Setser,[56] using the discharge flow–emission spectroscopy technique. They reported for $N_2(A\,^3\Sigma_u^+, v=0)$, $k=4.3\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.

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8. References

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