

## MEASUREMENTS OF THE RELATIVE RATE CONSTANTS FOR THE QUENCHING OF O(<sup>1</sup>D) ATOMS BY N<sub>2</sub>O AND N<sub>2</sub> AND THE BRANCHING RATIO OF THE N<sub>2</sub>O REACTION AT 23 AND -96 °C

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### Summary

The rate constant  $k_1$  for the quenching of O(<sup>1</sup>D) atoms by N<sub>2</sub>O relative to the rate constant  $k_2$  for the quenching by N<sub>2</sub> was determined by measuring the amount of NO produced as a function of the amount of N<sub>2</sub> added to constant flows of N<sub>2</sub>O in helium flowed through the photolysis cell. The high sensitivity of the chemiluminescence technique for NO measurement permitted very low conversions to be used. The ratio  $k_1/k_2$  was found to be 4.0 at 23 ± 2 °C and 2.9 at -96 ± 2 °C. The accuracy of these ratios is believed to be better than ±10%. The fraction  $k_{1a}/k_1$  of the reaction which produces NO

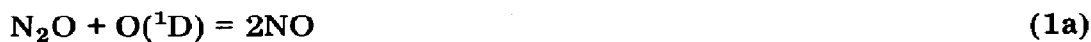


(with rate constant  $k_{1a}$ ) was determined by measuring the NO produced from the photolysis of N<sub>2</sub>O-helium mixtures in a flow system and the rate of pressure increase when the same mixture was photolysed in the cell under static conditions. The ratio  $k_{1a}/k_1$  was found to be 0.62 both at 23 ± 2 °C and at -96 ± 2 °C, with an uncertainty of ±15%. The branching fraction was found to be independent of the partial pressure of helium in contrast with other reports of a "hot atom" effect. The significance of these rate constant ratios to stratospheric chemistry is discussed.

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### 1. Introduction

Predictions of the impacts of human activity on atmospheric ozone are based on photochemical dynamic models. The sensitivities of these predictions to uncertainties in the rate constants for individual reactions have been tabulated in the recent reviews of the National Academy of Sciences [1] and of NASA [2]. The reaction of O(<sup>1</sup>D) atoms with N<sub>2</sub>O is reported to have one of the largest sensitivity factors. Any change in the accepted value for its rate constant would therefore result in a significant change in the model predictions. The reaction is known to have two major channels:



Since reaction (1a) is the main source of NO in the stratosphere, an important atmospheric parameter is the branching ratio of the two channels. In addition the O(<sup>1</sup>D) atoms, formed by photolysis of O<sub>3</sub> in the Hartley region, are rapidly quenched by collisions with the major atmospheric constituents, *e.g.*



It is therefore also important to have accurate values for the ratio of the rate constant for reaction (1a) to that of reaction (2). The sensitivity of the models to these rate constants stems not only from the direct role of NO as a chain carrier in the catalytic destruction of O<sub>3</sub> by the NO<sub>x</sub> family but also from its rapid reactions with the chain carriers in the ClO<sub>x</sub> and HO<sub>x</sub> catalytic cycles.

There have been a number of studies of the relative rate constants for the quenching of O(<sup>1</sup>D) by N<sub>2</sub>O and N<sub>2</sub>, *i.e.* of  $k_1/k_2$  (where  $k_1 = k_{1a} + k_{1b}$ ). These have been reviewed by Cvetanović [3] who reported a mean value of 4.4 for the various determinations with a standard deviation of about 30%. More recently there have been a number of studies [4 - 14] of the absolute quenching rate constants of O(<sup>1</sup>D) atoms with atmospheric gases. Some difficulties have been encountered in some of these studies, such as the use of a factor by Husain and coworkers [8 - 13] to correct for deviations from Beer's law in their resonance absorption technique and the occurrence of secondary emission observed by Davidson *et al.* [5] in their time-resolved 630 nm emission technique. These difficulties have been discussed in the NASA report [2]. In addition the agreement between Davidson *et al.* [7] and other groups for the rate constants of the reactions of O(<sup>1</sup>D) with halocarbons is better when they are referenced to N<sub>2</sub> and CO<sub>2</sub> than when they are referenced to N<sub>2</sub>O. There is a spread of a factor of 1.6 in the reported values of  $k_1/k_2$  from these absolute measurements.

There have also been a number of measurements of the branching fraction  $k_{1a}/k_1$ , the more recent of which are summarized in Table 1. O(<sup>1</sup>D) atoms were generated by photolysis of N<sub>2</sub>O or O<sub>3</sub> at a variety of wavelengths either in static or in flow experiments. The branching fractions were calculated from the ratios of two of the products N<sub>2</sub>, O<sub>2</sub> or NO. The reported branching fractions show a spread of about 20%. There has also been considerable disagreement regarding the dependence of the branching fraction on the presence of an excess of helium. Simonaitis *et al.* [17] were the first to report a small but measurable decrease in the fraction when excess helium was present, which they ascribed to a "hot atom" effect. Paraskevopoulos and coworkers [19, 21] failed to find such an effect in a series of studies. More recently Volltrauer *et al.* [16] and Davidson *et al.* [15] reported the observation of this effect while Marx *et al.* [20] did not observe it.

TABLE 1

A comparison of recently reported values of  $k_{1a}/k_1$ 

Reference	Wavelength (nm)	Gases analysed	$k_{1a}/k_1^a$
15	Continuum, 213.9	NO, O <sub>2</sub>	0.59 ± 0.02 0.56 ± 0.04 (He) <sup>b</sup>
16	184.9	NO, NO <sub>2</sub> , N <sub>2</sub>	0.58 ± 0.09 0.52 ± 0.06 (He)
17	213.9	N <sub>2</sub> , O <sub>2</sub> (indirect method)	0.61 ± 0.07 0.55 ± 0.08 (He)
18	Flash, > 230	NO <sub>2</sub> (indirect method)	0.59 ± 0.02
19	Flash	N <sub>2</sub> , NO	0.51 ± 0.08
20	184.9, 206.2	N <sub>2</sub> , O <sub>2</sub>	0.62 ± 0.02
This work	184.9, 253.7, 213.9, continuum with maximum at 235	NO ( $\Delta p$ ) <sup>c</sup>	0.62 ± 0.01

<sup>a</sup> The uncertainties are the authors' estimates of precision.<sup>b</sup> (He) refers to values obtained with excess helium. No helium effect was found by the last four investigators.<sup>c</sup> See Section 3.2.

In view of their importance to atmospheric chemistry we have undertaken a direct study of the ratios  $k_1/k_2$  and  $k_{1a}/k_1$  using a very direct and simple method requiring the monitoring of a single product, NO. These measurements were made at two temperatures spanning the range of atmospheric interest.

## 2. Experimental

The photolysis apparatus is shown schematically in Fig. 1. The photolysis cell used for the room temperature measurements consisted of a stainless steel tube, 3.5 cm in external diameter and 31.2 cm in length with Suprasil windows at each end. The temperature of the cell was maintained constant to within  $\pm 0.1$  °C by circulating thermostatted water from a 600 l reservoir through a coil of copper tubing soldered to the outer walls of the cell. The photolysis cell used for the low temperature measurements was of similar dimensions but was made of a Pyrex cylinder fitted with Suprasil windows. This cell was surrounded by dry ice contained in a Styrofoam box. The gas temperature in the cell was determined to be  $-96$  °C both by an internal calibrated thermocouple and by measuring the pressures of a given mass of gas in the cell at room temperature and when the cell was immersed in dry ice. To prevent condensation on the windows dry nitrogen, cooled to dry-ice temperature, was flowed across the windows through copper tubes loosely surrounding the windows and leading out of the Styrofoam box. The

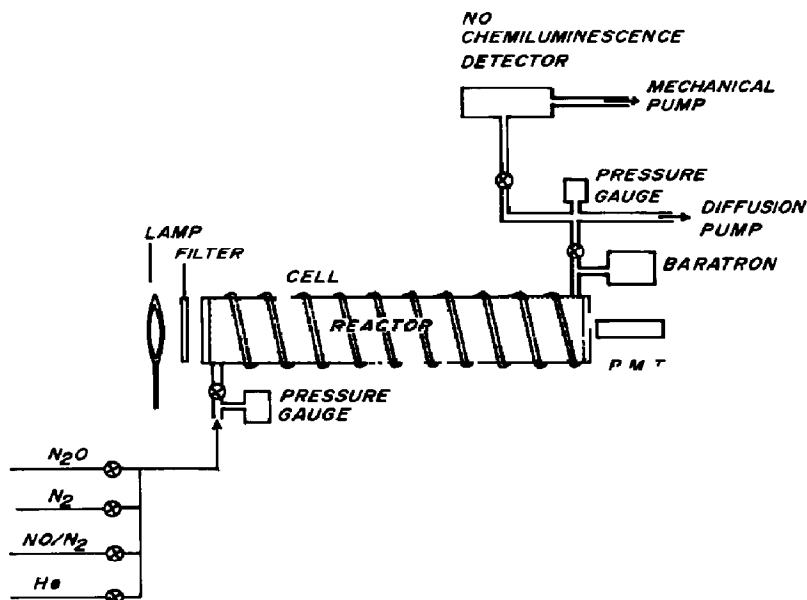


Fig. 1. A schematic diagram of the photolysis apparatus.

cells were connected to a mercury-free system. Known mixtures of helium buffer gas with  $N_2O$  and  $N_2$  were flowed through the cell. For the low temperature experiments the gas mixtures flowed through copper tubing 130 cm in length immersed in the dry-ice box before entering the cell. The flow rates of each of the gases were measured by Hastings mass flowmeters which were calibrated frequently during this study. The pressure in the cell was controlled by a valve at the outlet end of the cell and was measured with Wallace and Tiernan gauges. The total pressure in the cell was varied between 100 and 600 Torr and the residence time was varied from 0.67 to 4.6 s, corresponding to the photolysis of 0.01 - 0.1% of the  $N_2O$ .  $O(^1D)$  atoms were formed by photolysis of mixtures containing  $N_2O$  by one of three lamps: a Hanovia flat spiral mercury lamp, emitting mainly at 184.9 and 253.7 nm, a zinc lamp (Philips 93106) emitting at 213.9 nm and a deuterium lamp (Oriel 6316) emitting a continuum from 200 to 335 nm with maximum intensity at 235 nm. The constancy of the output of the lamps was monitored by a solar blind photomultiplier tube (P.M.T.). To prevent photolysis of NO by the 184.9 nm mercury line a cell containing NO at high pressure was inserted between the photolysis cell and the mercury lamp.

The photolysed gas was continuously flowed through a chemiluminescent NO analyser [22] having a sensitivity of  $100 \text{ counts (vol.ppb)}^{-1}$  and a detection limit of 20 vol.ppt. The zero reading for this instrument was obtained by blocking the radiation from the photolysis lamp. This zero signal was typically 1%, and never exceeded 10%, of the NO signal obtained during the photolysis. The instrument was calibrated for each experiment by the addition of known flows of NO to the unirradiated gas mixture, although

the experiments for the determination of  $k_2/k_1$  did not require knowledge of the absolute NO concentration.

The helium (Linde, rated purity 99.995%) was passed through silica gel at 77 K. The nitrogen (Matheson, rated purity 99.999%) was passed through a molecular sieve at 77 K.  $N_2O$  (Matheson, rated purity 99.99%) was passed over heated activated copper to remove oxygen and then was passed over activated charcoal and silica gel to remove NO and  $NO_2$ . Two gas mixtures were used to calibrate the chemiluminescence instrument. Their compositions were determined to be  $6.6 \pm 10\%$  and  $7.0 \pm 10\%$  vol.ppm of NO in  $N_2$  by comparison with laboratory standards and with mixtures prepared by flow dilution techniques. Frequent checks made throughout the course of this work showed that they maintained these compositions within the stated accuracies.

### 3. Results

#### 3.1. Determination of $k_1/k_2$

UV photolysis of  $N_2O$  at the wavelengths used in these experiments produces  $O(^1D)$  atoms:



These either undergo reaction (1) with  $N_2O$  or, in the presence of  $N_2$ , are quenched by reaction (2). The ratio of the NO concentration in the absence of  $N_2$  to that in the presence of  $N_2$  is given by the expression

$$\frac{[NO]_0}{[NO]} = 1 + \frac{k_2[N_2]}{k_1[N_2O]} \quad (A)$$

For constant  $N_2O$  flow a plot of the left-hand side of this expression against the  $N_2$  flow should be linear with a slope equal to  $k_2/k_1$ . An example of such a plot is given in Fig. 2. Similar linear plots, all with intercepts within 1% of unity, were obtained under a variety of conditions of total pressure,  $N_2O$  flow rates and residence times. These conditions and the calculated rate constant ratios at  $23 \pm 2^\circ C$  are given in Table 2. The average value of  $k_2/k_1$  was found to be 0.25 with a standard deviation of  $\pm 0.01$ . Results obtained with the three photolysis lamps were identical within the standard deviations obtained with each lamp. No differences were observed with or without the high pressure NO filter inserted between the photolysis cell and the mercury lamp, indicating that little NO photolysis occurs at 184.9 nm. The systematic errors involve only the flowmeter calibrations since these experiments do not require calibration of the chemiluminescent NO instrument other than to check that it responds in a linear fashion. Assessment of the systematic errors and standard deviations leads to an uncertainty estimate of  $\pm 10\%$ , i.e.  $k_2/k_1 = 0.25 \pm 0.03$ . The results obtained at  $-96^\circ C$  are shown in Table 3. At this temperature the value of  $k_2/k_1$  is  $0.34 \pm 0.04$ .

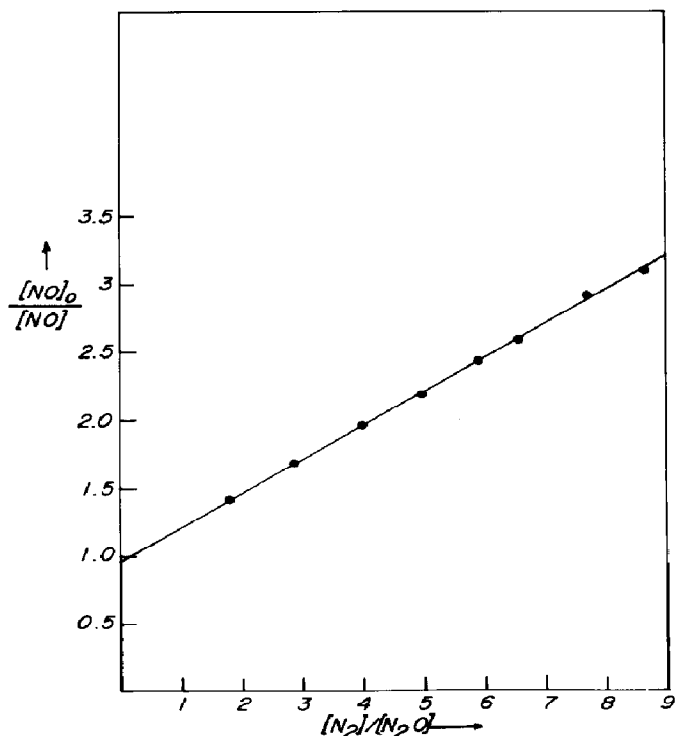


Fig. 2. A typical plot of the ratio of  $[NO]$  in the absence of  $N_2$  to that in the presence of  $N_2$  as a function of the  $[N_2]/[N_2O]$  ratio. For this example  $P_{N_2O} = 0.57$  Torr,  $P_{He} = 501$  Torr,  $T = 295 \pm 2$  K and the residence time = 2.09 s.

TABLE 2

Determination of  $k_2/k_1$  at  $23 \pm 2^\circ C$

$P_{N_2O}$ (Torr)	$P_{He}$ (Torr)	Residence time (s)	$k_2/k_1$
<i>Mercury lamp, 184.9 and 253.7 nm</i>			
0.72	606	2.42	0.27
0.20	176	0.71	0.25
0.47	461	1.85	0.26
0.27	264	1.07	0.25
0.15	128	0.52	0.24
0.50	433	1.76	0.26
0.15	175	0.71	0.26
1.24	401	1.62	0.26
0.30	100	0.40	0.25
0.60	208	0.82	0.25
1.27	460	1.84	0.26
0.54	133	0.53	0.25
1.11	607	2.42	0.26
1.36	589	2.34	0.27
0.90	463	1.85	0.27
0.21	114	0.47	0.24

TABLE 2 (continued)

$P_{\text{N}_2\text{O}}$ (Torr)	$P_{\text{He}}$ (Torr)	Residence time (s)	$k_2/k_1$
<i>Mercury lamp, 184.9 and 253.7 nm</i>			
0.65	425	1.77	0.24
1.02	616	2.57	0.26
0.83	535	2.19	0.26
1.42	533	2.20	0.26
1.00	440	1.86	0.25
0.32	201	0.82	0.25
<i>Deuterium lamp, continuum with maximum at 235.9 nm</i>			
1.03	560	2.28	0.26
0.48	247	1.02	0.25
0.71	398	1.64	0.26
0.71	381	1.59	0.25
0.97	383	1.60	0.26
1.65	384	1.62	0.26
0.22	381	1.60	0.26
0.27	131	0.55	0.23
0.55	94	0.39	0.24
0.56	690	2.94	0.25
0.70	324	1.35	0.24
1.22	514	2.15	0.25
0.95	525	2.14	0.25
1.69	524	2.14	0.25
0.24	125	0.52	0.24
1.08	578	2.38	0.26
1.08	579	2.39	0.25
0.46	365	1.52	0.24
<i>Zinc lamp, 213.9 nm</i>			
0.39	190	0.78	0.24
0.57	212	0.86	0.25
0.19	164	0.68	0.25
0.91	501	2.09	0.24
1.65	501	2.09	0.25
0.57	501	2.09	0.25
0.42	100	0.41	0.24
0.40	395	1.61	0.24
0.68	651	2.74	0.25
1.40	660	2.75	0.26
0.83	580	2.42	0.24

### 3.2. Determination of $k_{1a}/k_1$

In the absence of  $\text{N}_2$  the amount of NO formed during the residence time  $\tau$  is given by the expression

$$[\text{NO}] = (2k_{1a}/k_1)[\text{N}_2\text{O}] J\tau \quad (\text{B})$$

where  $J$  is the photolysis rate coefficient.

TABLE 3

Determination of  $k_2/k_1$  at  $-96 \pm 2^\circ\text{C}$ 

$P_{\text{N}_2\text{O}}$ (Torr)	$P_{\text{He}}$ (Torr)	Residence time (s)	$k_2/k_1$
<i>Mercury lamp at 184.9 and 253.7 nm</i>			
1.08	520	8.67	0.35
1.61	255	4.16	0.33
2.38	210	3.47	0.32
1.88	180	2.93	0.35
1.07	179	2.92	0.33
0.67	537	8.76	0.36
1.42	324	5.61	0.32

Experiments were performed, using the mercury lamp, in which the NO concentration was measured for a carefully controlled and measured flow of  $\text{N}_2\text{O}$  in helium. The residence time  $\tau$  could readily be calculated from the flow rates and the volume of the cell. The photolysis rate coefficient  $J$  was determined by closing the valves on either side of the cell, thus isolating it. Since reactions (3) and (1) produce three molecules of product for every two molecules of  $\text{N}_2\text{O}$  consumed, there will be a pressure rise  $\Delta p$  in the cell, which increases with time  $t$  according to the expression

$$\ln(1 - 2\Delta p/[\text{N}_2\text{O}]) = -2Jt \quad (\text{C})$$

The pressure increase was determined using a Baratron gauge and was recorded as a function of time on a strip chart recorder; an example of such a measurement is shown in Fig. 3. The bellows valves and the connecting tubing produced a dead volume of less than 2% of the photolysis volume. Typical photolysis times for these static experiments were of the order of 60 min during which time approximately 1% of the  $\text{N}_2\text{O}$  was photolysed. Temperature control was carefully maintained during the experiments. For a set of experiments with a given geometry the lamp intensity, as monitored using the phototube, and the  $J$  value obtained were constant within the experimental uncertainties. For a different geometry the lamp intensity and the  $J$  value both varied by the same factor. To ensure that the proper  $J$  value was used in expression (B) all the flow experiments were performed immediately after the  $J$  value determination.

Substitution of the  $J$  value obtained from the static experiments using expression (C) into expression (B) for the flow experiments gives the values for the branching fractions shown in Tables 4 and 5. The ratio  $k_{1a}/k_1$  was found to be 0.62 with a standard deviation of  $\pm 0.01$  both at  $23^\circ\text{C}$  and at  $-96^\circ\text{C}$ . Calibration errors in the flow rates, in the NO analysis and in the pressure measurements combine to give an uncertainty estimate of  $\pm 15\%$ , *i.e.*  $k_{1a}/k_1 = 0.62 \pm 0.08$ .



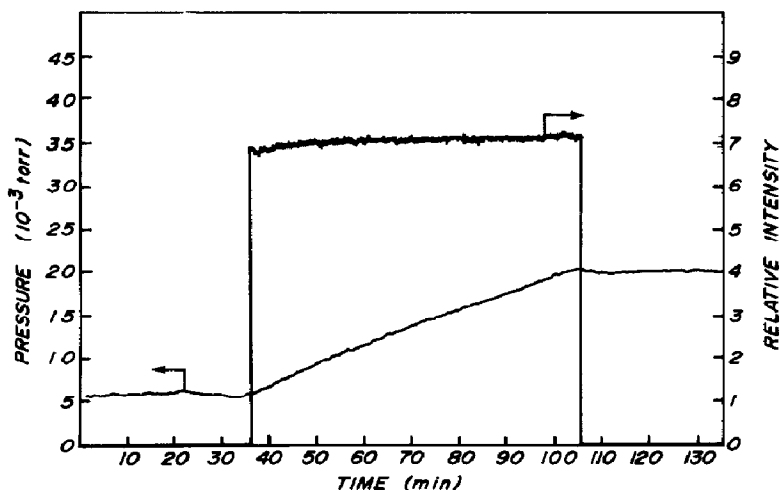


Fig. 3. A typical measurement of the pressure rise (left-hand ordinate) with time in a static experiment used to determine the photolysis rate coefficient  $J$ . The relative intensity (right-hand ordinate) is monitored by the photomultiplier to ensure constancy during the experiment. For this example  $P_{N_2O} = 0.91$  Torr and  $T = 295 \pm 2$  K.

TABLE 4

Determination of  $k_{1a}/k_1$  at  $23 \pm 2$  °C

$P_{N_2O}$ (Torr)	$[He]/[N_2O]$	Residence time (s)	$J$ ( $\times 10^{-6} s^{-1}$ )	$[NO]/[N_2O]$ ( $\times 10^{-6}$ )	$k_{1a}/k_1$
<i>Mercury lamp, 184.9 and 253.7 nm</i>					
0.91	—	1.41	3.87	6.73	0.62
1.25	—	0.66	3.83	3.12	0.62
1.80	—	1.60	4.16	8.22	0.62
2.32	—	1.75	3.83	8.32	0.62
2.26	—	2.23	3.37	9.18	0.61
0.84	9.2	4.61	3.54	19.90	0.61
1.60	5.1	0.92	3.45	3.91	0.62
0.79	—	2.77	3.62	12.23	0.61
0.92	—	3.78	3.75	17.31	0.61
0.90	—	2.74	4.42	15.25	0.63
1.77	—	2.27	4.32	11.95	0.61
0.95	8.9	0.49	4.21	2.57	0.62
2.12	—	1.50	3.82	7.21	0.63
1.83	3.1	1.66	4.04	8.19	0.61
1.32	5.7	2.36	4.06	12.09	0.63
1.36	—	3.91	4.15	19.45	0.60
1.69	4.3	1.91	3.77	8.80	0.61
1.89	—	1.84	4.17	9.21	0.60
1.44	5.3	2.78	4.28	14.75	0.62
0.88	9.4	1.69	4.52	9.45	0.62
1.77	4.0	1.76	5.01	10.74	0.61
2.20	—	2.71	4.85	16.31	0.62
1.66	—	3.55	4.90	20.86	0.60
0.98	8.5	1.89	4.65	10.74	0.61

TABLE 5

Determination of  $k_{1a}/k_1$  at  $-96 \pm 2^\circ\text{C}$ 

$P_{\text{N}_2\text{O}}$ (Torr)	Residence time (s)	$J$ ( $\times 10^{-6} \text{ s}^{-1}$ )	$[\text{NO}]/[\text{N}_2\text{O}]$ ( $\times 10^{-6}$ )	$k_{1a}/k_1$
<i>Mercury lamp, 184.9 and 253.7 nm</i>				
1.38	8.39	6.03	63.74	0.63
1.34	6.43	5.14	40.35	0.61
0.93	7.55	5.76	53.94	0.62
1.15	6.79	5.51	47.12	0.63
0.91	7.44	5.44	49.38	0.61

#### 4. Discussion

The ratio  $k_1/k_2$  of the overall rate constant for the reaction of  $\text{O}(^1\text{D})$  with  $\text{N}_2\text{O}$  to the quenching rate constant with  $\text{N}_2$  was found to be  $4.0 \pm 0.4$  at  $23 \pm 2^\circ\text{C}$ , which can be compared with the value of  $4.1 \pm 1.5$  recommended by Cvetanović [3] from an analysis of a large number of relative measurements. The ratio obtained from the absolute measurements of Heidner and coworkers [8 - 12] is  $3.2 \pm 0.4$ , that from the measurements of Davidson *et al.* [4] is  $3.9 \pm 1.1$  and that from the measurements of Amimoto *et al.* [14] is  $5.0 \pm 0.7$ . These groups of investigators have not been equally conscientious in distinguishing between the precision and the accuracy of their measurements. It is therefore difficult to assess whether the spread in the reported ratios lies within the range of the real uncertainties. Nor should the reported uncertainties be taken as indications of the relative accuracies of the measurements.

At  $-96 \pm 2^\circ\text{C}$  we find that the ratio  $k_1/k_2$  is  $2.9 \pm 0.4$ . Davidson *et al.* [15] found that  $k_1$  was independent of temperature while  $k_2$  had a small negative temperature dependence. The value of  $k_1/k_2$  at  $-96^\circ\text{C}$  calculated from their results is  $3.0 \pm 0.8$ , which is in excellent agreement with our value.

A comparison between our determination of  $k_{1a}/k_1$  for the reaction of  $\text{O}(^1\text{D})$  with  $\text{N}_2\text{O}$  and values reported in the recent literature is given in Table 1. The sources of  $\text{O}(^1\text{D})$  atoms included photolysis of  $\text{N}_2\text{O}$ ,  $\text{O}_3$  and  $\text{NO}_2$  at a variety of wavelengths. With the exception of this study and that of Davidson *et al.* [15] all the photolyses were conducted in static systems. Aside from the indirect method of Ghormley *et al.* [18] all the other methods required the analyses of two of the photolysis products in contrast with our method which required only the measurement of a single product,  $\text{NO}$ , and a pressure change. The values of the ratio range from 0.50 to 0.62. Although this range exceeds the sum of the standard deviations reported by various authors it might not exceed the sum of the uncertainties if systematic errors in the measurements were also included. A value of 0.50 for the ratio was adopted for the models used in the National Academy of Sciences report [1] while a ratio of 0.56 was recommended in the NASA report [2].

In a recent critical evaluation from the Jet Propulsion Laboratory [23] a value of 0.54 based on the results of Davidson *et al.* [15] and of Volltrauer *et al.* [16] is recommended. The evaluated uncertainty at the  $1\sigma$  level for each of  $k_{1a}$  and  $k_{2a}$  was given as 30%.

There do, however, appear to be real differences regarding the effect of excess helium on the branching fraction. Investigators in three laboratories in the U.S.A. have all found small but significant decreases in the branching fraction in the presence of excess helium, while investigators in laboratories in Canada and in the F.R.G. have not. We failed to see such an effect over the range of helium-to-N<sub>2</sub>O ratios from 0 to 9.4. The total pressure in our experiments was lower than those of the other investigators, never exceeding 10 Torr. Since the reaction of O(<sup>1</sup>D) with N<sub>2</sub>O does not occur with unit collision efficiency any "hot atom" would be expected to become more evident the lower the pressure. However, if the observed effect is a result of quenching of O(<sup>1</sup>D) by impurities in the helium, it might become more evident at higher pressures. At this time we offer no other explanation for the apparent "latitude" dependence of the helium effect.

Tully [24] has reported a theoretical value for the branching fraction. The rate of formation of a particular product is assumed to be proportional to the density of states at some "critical configuration" multiplied by the probability that, once attained, the critical configuration will decompose to that product. Other assumptions include the absence of any barriers limiting the close approach of the reactants and the operation of the non-crossing rule in construction of the correlation diagrams connecting reactant and product states. Tully [24] derived a value of 0.63 for  $k_{1a}/k_1$ . No great satisfaction can be gained, however, by the agreement with the value obtained in this work since the same theoretical treatment gives considerable branching for reactions of O(<sup>1</sup>D) with CO<sub>2</sub> and with H<sub>2</sub>O; the first of these reactions has now been shown [25] to proceed exclusively by physical quenching and the second reaction [26] by chemical reaction to form HO. Wiesenfeld [27] has suggested that this discrepancy might be removed if the non-crossing rule is relaxed but he has not calculated the branching fractions.

For atmospheric modelling the important ratio is  $k_{1a}/k_2$ . The ratio obtained from our measurements is  $2.5 \pm 0.3$  at 23 °C. The value which can be calculated from the rate constants recommended in the NASA report [2] at this temperature is  $2.1 \pm 0.9$ . The corresponding value from the rate constants recommended in the Jet Propulsion Laboratory evaluation [23] is  $2.0 \pm 0.9$ . The predicted value for the ozone depletion caused by halocarbon releases is, according to the National Academy of Sciences report [1], sensitive to the value of  $k_{1a}$  by a factor  $r = -0.43$ , *i.e.* a 1% change in the selected value of  $k_{1a}$  results in a 0.43% change in the predicted ozone depletion. The corresponding value of  $r$  in the analysis given in the NASA report [2] is  $-0.429$ . If similar sensitivity factors apply to the  $k_{1a}/k_2$  ratio, then the choice of our value of 2.5 rather than the value of 2.1 recommended in the NASA report [1] would have changed the predicted ozone depletion by 8% of the values given in those reports [1, 2].

The uncertainty  $u$  in the predictions of the ozone depletion due to the uncertainty  $f$  in the rate constant of a given reaction is given by  $u = 2f \ln r$ . The reduction in uncertainty of  $k_{1a}/k_2$  from the recommended value of  $\pm 0.9$  to our value of  $\pm 0.3$  would therefore reduce the uncertainty due to these reactions by a factor of 3.

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