

Absolute rate constants for the reaction $O(^3P) + NO_2 \rightarrow NO + O_2$ over the temperature range 230–339°K*

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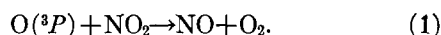
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Using the technique of flash photolysis–resonance fluorescence, absolute rate constants have been measured for the reaction $O(^3P) + NO_2 \rightarrow NO + O_2$. Over the temperature range 230–339°K, the rate constant was found to have the value $k = 9.12 \pm 0.44 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, independent of temperature. At stratospheric temperatures, this rate constant is about a factor of two faster than indicated from previous measurements.

INTRODUCTION

The interaction of the nitrogen oxides, NO and NO₂, with atomic oxygen and ozone has been proposed as an important factor in establishing the observed concentrations of stratospheric ozone.^{1–3} One of the important reactions in the proposed mechanism is the bimolecular reaction of atomic oxygen in its ground electronic state with nitrogen dioxide:



The need for accurate kinetic data on this reaction at stratospheric temperatures and pressures has been emphasized more recently by the suggestion that nitrogen oxides emitted by a large fleet of supersonic aircraft might significantly reduce the ozone concentration in the stratosphere.^{4,5}

There have been several determinations of the rate constant for Reaction (1).^{6–14} These results have recently been reviewed by Baulch, Drysdale, and Horne.¹⁵ Because of the scatter in these data when displayed on a single Arrhenius plot, the authors¹⁵ consider their recommended value to be reliable only to within $\pm 20\%$ over the temperature range 280–550°K. There are no reported values for the rate constant below ice temperatures which, when coupled with the large scatter in the data over the measured temperature range, means that any extrapolation of the rate constant for $O + NO_2$ to stratospheric temperatures ($\sim 220^\circ\text{K}$) could be subject to large errors.

Since the reaction of ground state atomic oxygen with nitrogen dioxide is now thought to be of critical importance to the further understanding of stratospheric chemistry, we have undertaken a flash photolysis–resonance fluorescence study in an effort to better establish the rate parameters for this reaction at stratospheric temperatures.

EXPERIMENTAL

The flash photolysis–resonance fluorescence technique used in this study has been discussed in detail previously.^{16,17} In these experiments, a mixture consisting of 1–7 mtorr of NO₂, 1 torr of oxygen and ~ 4 torr of a diluent gas (Ar, N₂, O₂, and CO₂) was flash photolyzed above $\lambda = 1050 \text{ \AA}$, producing on the order of 0.05 to 0.005 mtorr of atomic oxygen. A small portion of the atomic oxygen was continuously excited by an atomic oxygen resonance lamp, and the decay of oxygen atoms in the mixture was monitored by following the fluorescence of the atomic oxygen resonance radiation. The fluorescence signal was recorded on a multichannel analyzer, and multiple flashes (> 100) were used to generate one kinetic decay curve. The reaction mixture was changed several times in the course of an experiment to prevent a significant depletion of the NO₂ ($> 5\%$). These experiments were conducted with the concentration of NO₂ in great excess over that of atomic oxygen, so that first-order loss of atomic oxygen prevailed. The first order rate constant was determined from a plot of the logarithm of the count rate, corrected for background, against channel number, or time. A good linear fit was found over at least a full decade change in the count rate. This first order rate constant was corrected for loss of atomic oxygen due to reaction with molecular oxygen, and to diffusion from the reaction zone, and was then used to derive the bimolecular rate constant for the reaction by dividing by the NO₂ concentration. The combined correction indicated above typically was less than 15% of the total first order rate constant.

The oxygen and argon used in this work were Matheson Ultra-High Purity Gold Label¹⁸ and the nitrogen was Air Products Ultra-High Purity¹⁸ (all better than 99.999% stated purity). These gases were

used without further purification. Matheson CO_2 was purified by outgassing at 77°K. Matheson nitrogen dioxide was used after being mixed with a few hundred torr of oxygen to remove the residual nitric oxide. Repeated degassing at 195 and 77°K were then used to remove the O_2 . An infrared analysis of the treated NO_2 gas showed no evidence of NO being present (<1%).

In the preparation of reaction gas mixtures, low pressures (0.05–5 torr) were measured using a Granville-Phillips capacitance manometer,¹⁸ calibrated against a dibutyl phthalate manometer. Higher pressure measurements were made on a two-turn Bourdon gauge. The precision to which various gas mixtures could be made up was determined to be ~3%.

In the previous flash photolysis-resonance fluorescence work in this laboratory, a brass reaction cell was employed. During this study, however, it was observed that with the brass reaction cell, the measured rate constant decreased at temperatures above 298°K. At 298°K and above, the rate constant also depended on the length of time the reaction mixture was in contact with the cell before the experiment was carried out. This decrease in the rate constant was attributed to the decomposition of NO_2 on the walls of the reaction cell at those temperatures. This effect was not found to be important below room temperature.

Because of the uncertainties caused by NO_2 decomposition in the brass cell, an all glass reaction vessel was constructed (see Fig. 1). The all glass reaction vessel was approximately 30 cm³ in volume and had one window port on each of the principal axes of the cell. These window ports were aligned with the vacuum uv flash lamp, atomic resonance lamp, and the photon detector (electromagnetic multiplier). Low temperature cycling of the cell was achieved by snugly fitting a copper jacket to the walls of the reaction cell through which precooled nitrogen gas was circulated. For high temperature operation resistive heating elements were installed in the copper jacket. The temperature was

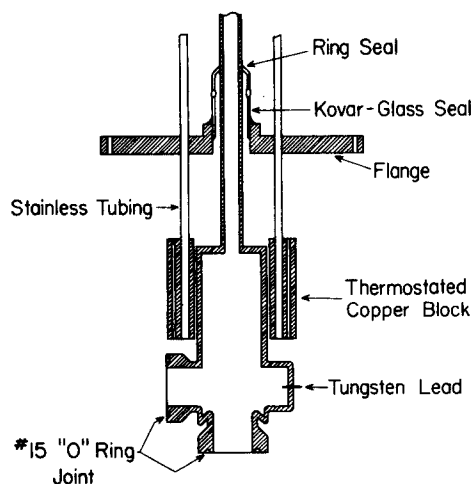


FIG. 1. Schematic drawing of glass reaction cell.

measured using a thermocouple junction which was spot welded to a tungsten rod embedded directly into the walls of the cell. To test for temperature equilibration between the glass reaction vessel and the gas mixture within this cell, rate constants were measured for the reaction of $O(^3P)$ with ethylene at both high and low temperatures. In each case the rate constants measured in the glass cell agreed with those previously measured in the brass reaction vessel¹⁶ to within 2%–3%.

In those measurements carried out in the glass cell, the rate constant for Reaction (1) was always found to be independent of the length of time that the NO_2 was in contact with the cell (up to at least 15 min).

In addition to the problems encountered from NO_2 decomposition on the walls of the brass reaction cell, it was observed that NO_2 underwent significant photolysis by room (fluorescent) lights. Purified NO_2 was stored, therefore, in a blackened glass bulb and all mixing bulbs on the gas handling system were covered with black shrouds.

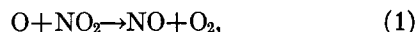
The low temperature limit at which the kinetics of the $O(^3P) + NO_2$ reaction could be studied was determined by dimer formation arising from the equilibrium:



At 230°K and 5 mtorr NO_2 , calculations of the N_2O_4 concentration using the equilibrium constant¹⁹ indicated that approximately 0.4 mtorr of N_2O_4 would have been present, representing about an 8% loss of NO_2 . At 220°K, there would have been about a 50% loss of NO_2 . In this work, therefore, all kinetic measurements were made at temperatures of 230°K or higher. (It should be noted that because of the much lower concentrations of NO_2 in the stratosphere, $\sim 10^{-2}$ – 10^{-4} mtorr, >99% of the NO_2 at 220°K would be in the monomer form.)

RESULTS AND DISCUSSION

The rate constant for Reaction (1),



was measured over the temperature range of 230 to 339°K. The results of these measurements are listed in Tables I and II, and are plotted in Arrhenius form in Fig. 2. A least squares fit of all of the data to the Arrhenius equation resulted in the expression:

$$k_1 = 8.70 \pm 0.65 \times 10^{-12} \times \exp[(26 \pm 41 \text{ cal mol}^{-1})/RT] \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}.$$

The error limits in this expression are the standard errors from the least squares treatment of the data. The uncertainties calculated from a consideration of the lines with the maximum and minimum slopes which could be drawn through the attached error bars ($\pm 4\%$) are $\pm 2.5 \times 10^{-12}$ cm³ molecule⁻¹·sec⁻¹ in the pre-exponential factor and ± 150 cal mol⁻¹ in the activation energy.

TABLE I. Rate measurements on the reaction $O(^3P) + NO_2 \rightarrow NO + O_2$ at 298°K.^a

NO ₂ mtorr	Diluent ^b	Reaction cell	Flash window	Flash energy (J)	First order <i>k</i> (sec ⁻¹)	Bimolecular <i>k</i> × 10 ¹² (cm ³ molecule ⁻¹ ·sec ⁻¹)
...	Ar	Glass	LiF	40	132	
1.10	Ar	Glass	Sapphire	65	445	8.79
1.37	Ar	Glass	LiF	30	547	9.39
1.88	Ar	Glass	LiF	45	654	8.62
2.09	Ar	Glass	LiF	35	736	8.74
2.15	Ar	Glass	Sapphire	65	811	9.93
2.16	Ar	Glass	LiF	30	665	8.84
2.22	Ar	Glass	Sapphire	65	786	9.17
2.76	Ar	Glass	Sapphire	60	912	8.77
2.77	Ar	Glass	LiF	18	1016	9.90
2.77	Ar	Glass	LiF	85	962	9.30
3.18	Ar	Glass	Sapphire	65	1038	8.83
4.09	Ar	Glass	LiF	30	1361	9.32
6.96	Ar	Glass	Sapphire	65	2150	8.95
...	N ₂	Glass	Sapphire	65	118	
2.17	N ₂	Glass	Sapphire	65	771	9.30
2.18	N ₂	Glass	Sapphire	65	800	9.65
2.20	N ₂	Glass	Sapphire	65	820	9.80
...	O ₂	Glass	Sapphire	65	127	
2.20	O ₂	Glass	Sapphire	65	740	8.60
2.21	O ₂	Glass	Sapphire	65	799	9.38
...	CO ₂	Glass	Sapphire	65	124	
3.16	CO ₂	Glass	Sapphire	65	997	8.53

^a All experiments were performed using 1 torr of oxygen.

^b The total pressure for each of the diluent gases was 5 torr.

As is evident from the Arrhenius expression, the rate constant is, within experimental uncertainty, independent of temperature. A simple average of all of the data from the tables gives, as a temperature independent rate constant,

$$k_1 = 9.12 \pm 0.46 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1},$$

where the stated uncertainty is now the standard deviation of the data points from the mean. This value is within the standard error of the Arrhenius expression over the entire temperature range.

At 298 and 339°K, the kinetic data reported were measured using the glass reaction cell. The kinetic data taken using the brass cell at these temperatures were unreliable due to NO₂ decomposition. Since decomposition was not important at the lower temperatures (below 298°K) data obtained with both the brass and the glass reaction cells were used. Identical answers, within experimental error, were obtained using the two cells at these temperatures. In these experiments the total pressure was limited to 5 torr to prevent a significant contribution to the measured rate from the fast third order combination reactions, between O and NO₂.

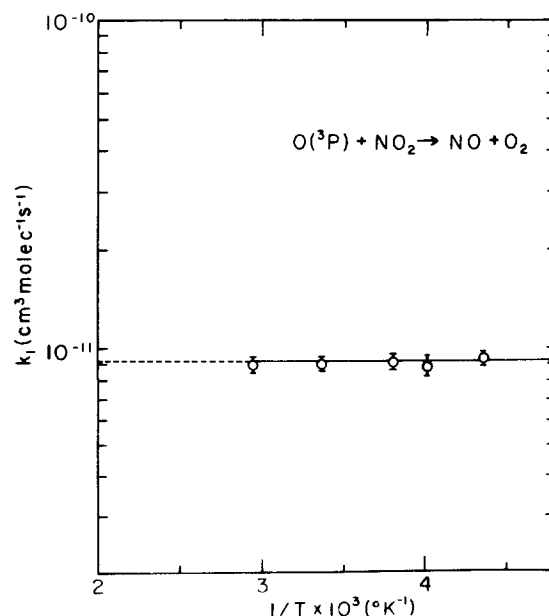


Fig. 2. Arrhenius plot for the reaction $O(^3P) + NO_2 \rightarrow NO + O_2$. The error bars on each temperature point represent one standard deviation calculated from averaging all *k* values measured at a single temperature.

TABLE II. Rate measurements on the reaction $O(^3P) + NO_2 \rightarrow NO + O_2$.^a

T ($^{\circ}K$)	NO_2 mtorr	Diluent ^b	Reaction cell	Flash window	Flash energy (J)	First order k (sec^{-1})	Bimolecular $k \times 10^{12}$ (cm^3 molecule ⁻¹ $\cdot sec^{-1}$)
230	...	N ₂	Brass	LiF	35	88	
230	2.77	N ₂	Brass	LiF	35	1179	9.40
230	...	Ar	Brass	LiF	45	83	
230	1.08	Ar	Brass	LiF	35	486	8.85
230	2.71	Ar	Brass	LiF	18	1246	10.2
230	2.71	Ar	Brass	LiF	30	1088	8.86
230	2.71	Ar	Brass	LiF	95	1052	9.35
230	4.34	Ar	Brass	LiF	35	1838	9.65
246	...	Ar	Glass	Sapphire	60	78	
246	1.38	Ar	Glass	Sapphire	60	574	9.18
246	2.75	Ar	Glass	Sapphire	60	965	8.05
246	4.10	Ar	Glass	Sapphire	60	1530	9.05
263	...	Ar	Glass	Sapphire	60	124	
263	1.38	Ar	Glass	Sapphire	50	627	9.96
263	2.68	Ar	Glass	Sapphire	60	955	8.46
263	2.75	Ar	Glass	Sapphire	50	861	8.56
263	2.76	Ar	Glass	Sapphire	60	912	8.77
263	2.72	N ₂	Brass	LiF	40	1040	9.26
263	2.71	Ar	Brass	Sapphire	60	1040	9.19
263	2.71	Ar	Brass	LiF	40	1050	9.26
339	...	Ar	Glass	Sapphire	65	157	
339	1.35	Ar	Glass	Sapphire	65	503	8.96
339	2.66	Ar	Glass	Sapphire	65	862	9.31
339	5.35	Ar	Glass	Sapphire	65	1457	8.55

^a All experiments were performed using 1 torr of oxygen.

^b The total pressure for each of the diluent gases was 5 torr.

Recent results from our laboratory indicate that the third order reaction would not have influenced the measurement of the bimolecular rate constant by more than 2% at the operating pressure of 5 torr.²⁰

At several temperatures, both LiF and sapphire were used as flash lamp windows. It was found that within the experimental error of the measurements no effect on the rate constant was observed. As discussed earlier,¹⁶ this would indicate that the production of $O(^1S)$ was not complicating the reported rate measurements. In most of the rate measurements of Reaction (1), Ar was used as the diluent gas. At 298°K, however, N₂, O₂, and CO₂ were also used (Table I). At several other temperatures, both N₂ and Ar were employed (Table II). Within the experimental scatter of the data, no dependence of the measured rate constant on the nature of the diluent gas was observed, thus indicating that only the simple bimolecular Reaction (1) was being studied. In addition, the lack of a dependence on the diluent gas shows that the system was not complicated by secondary reactions involving $O_2(^1\Sigma_g)$, produced by the quenching of $O(^1D)$. This point has been discussed in detail elsewhere.^{16,17} Reactions of hot atoms formed in

the primary photolytic process can also be discounted in this work since the number of collisions with the diluent gas was over 1000 times greater than with the reactant NO₂. Under these conditions, temperature equilibration of the O atoms would be insured.

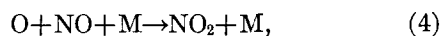
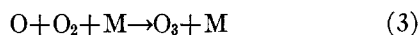
In order to determine if other possible secondary reactions were complicating the kinetic measurements, the flash intensity, and therefore the atom concentration, was varied by a factor of five at both 298°K and 230°K. Also, the NO₂ concentration was varied by a factor of four at 230°K, and by a factor of six at 298°K. As seen in Table I, neither the variation in the atomic oxygen nor the NO₂ concentration resulted in a change in the measured rate constant outside of the experimental error. These measurements would indicate, therefore, that secondary reactions involving other reactive species produced by the flash or products from the primary reaction were of negligible importance in this study. A more extensive discussion of other possible systematic errors associated with the measurement of rate constants using the flash photolysis-resonance fluorescence technique can be found in previously reported studies.^{16,17}

TABLE III. Summary of reported rate measurements on the reaction $O(^3P) + NO_2 \rightarrow NO + O_2$.

T ($^{\circ}K$)	k ($cm^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)	Reference
230–339	9.12×10^{-12} (Temperature independent)	This work
300	1.0×10^{-11}	Ford and Endow ⁶
298	1.4×10^{-11}	Schuck, Stephens and Schrock ⁷
298	3×10^{-11}	Nutt and Biddlestone ⁸
298	2.5×10^{-12}	Phillips and Schiff ⁹
278–375	$3.24 \times 10^{-11} \exp[(-1060 \text{ cal mol}^{-1})/RT]$	Klein and Herron ¹⁰
298	5.41×10^{-12}	
297–543	$1.7 \times 10^{-11} \exp[(-580 \text{ cal mol}^{-1})/RT]$	Westenberg and deHaas ¹¹
298	6.26×10^{-12}	
298	8.3×10^{-12}	Clyne and Cruse ¹²
298	5.6×10^{-12}	Smith ¹³
410	8.1×10^{-12}	Smith ¹³
298	4.4×10^{-12}	Stuhl and Niki ¹⁴
280–550	$1.7 \times 10^{-11} \exp[(-600 \text{ cal mol}^{-1})/RT]$	Baulch, Drysdale, and Horne ¹⁵ (evaluation)

COMPARISON OF RESULTS

A comparison of the present results with those of previous studies is given in Table III. One of the first quantitative measurements of the rate constant for Reaction (1) was carried out by Ford and Endow⁶ in a study of the photolysis of NO_2 at 3660 Å. By observing the effects of small additions of nitric oxide and oxygen on the quantum yield for NO_2 decomposition, they were able to obtain rate constants relative to the Reactions (3) and (4),



where $M = N_2$.

Schuck, Stephens, and Schrock⁷ also studied the NO_2 photolysis with added O_2 and NO and obtained relative rate constants for Reaction (1) with $M = O_2$. Using the results from this laboratory¹⁷ for k_3 with $M = N_2$, and the results of Kaufman and Kelso²¹ with $M = O_2$, these relative rate data were put on an absolute basis and are included in Table III. The rate constant derived from the results of Ford and Endow⁶ is in excellent agreement with the present value for k_1 (within 10%). The agreement with the value derived from the data of Schuck, Stephens, and Schrock⁷ is less satisfactory (~50%), but is not unreasonable considering the experimental errors associated with the two measurements of k_1 and the uncertainty in Kaufman and Kelso's value (~15%) for k_3 (for $M = O_2$).

Using a mass spectrometric technique, Nutt and Biddlestone⁸ were able to derive an estimate of the collision efficiency of Reaction (1). In this investigation, the reaction was studied by flowing a beam of atomic oxygen through a chamber containing a low pressure of NO_2 . The beam then passed into the ionization chamber of a mass spectrometer, and the relative peak heights with and without the discharge on were used to cal-

culate a collision efficiency of about 0.2 to 0.25. The value of k_1 listed in Table III was calculated using a collision frequency of $1.3 \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$ for atomic oxygen and nitrogen dioxide (collision diameter of 4 Å). Since the experiment gave only an approximate measurement of the collision efficiency, the agreement to within only a factor of three is not unreasonable.

Both Phillips and Schiff⁹ and Klein and Herron¹⁰ used discharge-flow systems coupled to mass spectrometers to determine rate constants for the reaction of atomic oxygen with nitrogen dioxide. In both studies atomic oxygen was generated either by a discharge in a few percent O_2 in Ar or by means of the Reaction (5) $N + NO \rightarrow N_2 + O$. Phillips and Schiff obtained a room temperature rate constant almost a factor of four lower than the value reported here. Klein and Herron¹⁰ on the other hand, reported a rate constant of 298°K which was about half of the value measured in this work. The activation energy reported by these authors¹⁰ for Reaction (1) was 1060 cal mol⁻¹, but the scatter in their data was $\sim \pm 20\%$. Although it is not completely clear why the discharge flow-mass spectrometry results are lower than those reported in this work, the large decrease in the bimolecular rate constant observed by Klein and Herron¹⁰ at temperatures below 260°K would tend to indicate that one or more side reaction(s) were complicating the kinetic analysis. If similar processes were also significant at 298°K, this might explain the lower values of the rate constant obtained by both Klein and Herron¹⁰ and Phillips and Schiff⁹ at that temperature.

Westenberg and deHaas¹¹ also measured the temperature dependence of the rate constant for Reaction (1) using a discharge flow system. In this case, atom detection was by esr. They combined their data with those of Klein and Herron¹⁰ to obtain the Arrhenius parameters given in Table III. Their data, however,

showed little apparent temperature dependence and gives an average value of $k_1 = 8.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$, which is within 15% of the present temperature independent rate constant.

In a recent investigation by Clyne and Cruse,¹² the rate constant for Reaction (1) was determined at 298°K using a discharge-flow system. Atomic oxygen was produced by Reaction (5) and the atom concentration was monitored by the absorption of the atomic resonance radiation. The rate constant reported in that study is within 10% of the present value.

There have been two flash photolysis studies of the $O + NO_2$ reaction.^{13,14} Smith¹³ used NO_2 as the atom source and measured the rate constant relative to Reaction (6) $O + CS_2 \rightarrow CS + SO$. The 298°K rate constant measured by Smith was almost a factor of two lower than that reported in this work, and, in addition, it was observed to be temperature dependent. The measurement of k_1 reported by Smith,¹³ however, is based on Smith's¹³ measured value of k_6 . If the reaction of atomic oxygen with 1-butene²² is used as a reference reaction, instead of Reaction (6), Smith's relative rate constants give values for k_1 of 7.37×10^{-12} and $9.15 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$ at 298 and 410°K, respectively. These values agree with those reported here within the stated experimental uncertainties ($\pm 30\%$) of Smith's work.

Stuhl and Niki¹⁴ flash photolyzed NO to produce oxygen atoms and monitored the atom decay using the $O + NO$ chemiluminescence reaction. The rate constant for Reaction (1) was determined from the increase in the decay rate upon addition of NO_2 . This measurement of k_1 resulted in a rate constant a factor of two lower than that reported here. The reactor used in this study was a 17 liter stainless steel chamber. The reactants were allowed to mix in the reactor and were

therefore in contact with it for a long period of time. It is possible, therefore, that their results reflect the effect of decomposition of NO_2 on the surface of their reactor. As observed in the present work, the presence of certain metal surfaces can result in a lower value for the rate constant.

CONCLUSIONS

One of the principal reasons for studying the kinetics of the reaction of atomic oxygen with nitrogen dioxide, is to obtain further insight into the role that the nitrogen oxides might play in defining the ozone concentration profile of the stratosphere. The effect of Reaction (1) on the ozone balance is related in part to the magnitude of k_1 , compared to the rate constant of the ozone forming Reaction (3),



In previous work for this laboratory,¹⁷ the rate constant for Reaction (3) was found to be about factor of two lower at stratospheric temperatures than the previously recommended value for k_3 .²³ In the present work, the rate constant for Reaction (1) was found to be a factor of two higher at stratospheric temperatures than the value extrapolated from the previously recommended¹⁵ rate expression for k_1 at temperatures above 280°K. This means that the ratio k_3/k_1 is a factor of four lower than the value used in previous modeling calculations.^{2,4} This new ratio for k_3/k_1 would seem to indicate that the amount of nitrogen oxide necessary to explain the experimentally observed stratospheric ozone profile might be as much as a factor of four lower than previous estimates. It is expected that this new ratio of k_3/k_1 would also be of considerable importance to the future evaluation of the possible effects of supersonic aircraft on the ozone balance.

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