

## O(<sup>1</sup>D)/N<sub>2</sub>O BRANCHING RATIO AT 290 K

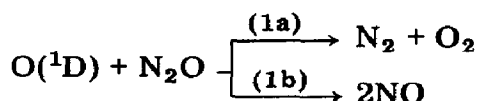
HERMANN N. VOLLTRAUER, WILLIAM FELDER, ROBERT J. PIRKLE\*, and ARTHUR FONTIJN

AeroChem Research Laboratories, Inc., P.O. Box 12, Princeton, N.J.08540 (U.S.A.)

(Received January 18, 1979)

### Summary

The branching ratio  $k_{1a}/k_{1b}$  for



has been measured. O(<sup>1</sup>D) was produced from N<sub>2</sub>O photolysis at 184.9 nm. The photolyses were carried out at [N<sub>2</sub>O] = 9.6 × 10<sup>17</sup> to 4.3 × 10<sup>18</sup> ml<sup>-1</sup> and [He] = 0 or 2.1 × 10<sup>19</sup> to 2.4 × 10<sup>19</sup> ml<sup>-1</sup>. The product N<sub>2</sub> was determined by gas chromatography; NO and its oxidation product NO<sub>2</sub> were each determined with a chemiluminescence analyzer. The measurements yield  $R_0 = 0.73 \pm 0.11$  and  $R_{\text{He}} = 0.92 \pm 0.10$  for "hot" and for thermally modified (with He) O(<sup>1</sup>D), respectively. These error limits pertain to accuracy. Exclusion of systematic errors common to both sets of experiments leads to  $R_0/R_{\text{He}} = 0.80 \pm 0.10$ , indicative of a definite effect of the O(<sup>1</sup>D) kinetic energy on the branching ratio. Analysis of these and previous data suggests good agreement within realistic error limits.

### 1. Introduction

The reaction of O(<sup>1</sup>D) with N<sub>2</sub>O



is thought to be the predominant source of NO in the natural stratosphere and hence it is important in controlling [O<sub>3</sub>] in that environment [1]. The overall reaction (1) proceeds rapidly ( $k_1 = 1.1 \times 10^{-10}$  ml molecule<sup>-1</sup> s<sup>-1</sup> [2]) while other reaction paths, such as deactivation [3] to O(<sup>3</sup>P) and formation [4] of N + NO<sub>2</sub>, have been shown to account for less than 4% of

\*Present address: Gulf Oil Research Center, Blaw Knox, Pa., U.S.A.

the reaction events. As a result considerable interest has centered on an accurate determination of  $R = k_{1a}/k_{1b}$ .

$R$  has been determined in a number of experiments using  $O(^1D)$  derived from UV photolysis of suitable parent molecules ( $N_2O$ ,  $NO_2$ ,  $O_3$  and  $O_2$ ). These experiments have led to apparently conflicting results. Several investigators [4, 5] have found that  $R \approx 1$  but others [6, 7] suggest  $R \approx 0.7$ . It has been suggested [7] that this difference in  $R$  is related to "thermalization" of the originally translationally hot  $O(^1D)$  formed in the photolysis; indeed Heicklen's group showed [7] that the addition of helium to thermalize the  $O(^1D)$  led to an increase in  $R$  from 0.65 to 0.83. However, Wiebe and Paraskevopoulos (WP) [4] obtained the same value of  $R$  both from translationally hot  $O(^1D)$  and from  $O(^1D)$  thermalized by helium and neon; Preston's results [5] also suggest no kinetic energy effect on  $R$ . Work from the same laboratory moreover suggests [8] that the  $O(^1D)$  may, in most of these measurements, have been only partially thermalized; "thermally modified"  $O(^1D)$  thus appears to be a more appropriate expression here.

In view of these small, but possibly significant, discrepancies in measurements of  $R$ , further careful work, in which considerable attention is given to defining the accuracy of the results and in which additional experimental methods are applied to the problem, is needed. The present work is one such approach. In this work  $N_2$  and  $NO$  from



followed by reaction (1) are measured. The method of analysis used allows measurement of both  $[NO]$  and  $[NO_2]$  after the photolysis (their sum corresponds to the total  $[NO]$  formed in reaction (1b)) and is thus independent of subsequent reactions. A chemiluminescence  $NO/NO_x$  ( $= NO + NO_2$ ) analyzer [9, 10] based on the  $NO/O_3$  chemiluminescent reaction was used for this analysis. Our findings, like those of the earlier work, pertain to room temperature. The  $R$  values obtained have been reported in preliminary form [11]. Simultaneously with this work a mass spectrometric study was performed by Davidson *et al.* [12] which included measurements from 170 to 434 K. For 290 K their  $R$  values are  $0.68 \pm 0.11$  for photolysis of pure  $N_2O$  and  $0.79 \pm 0.13$  for  $[He] \geq 10[N_2O]$ .

## 2. Experimental

### 2.1. Apparatus and method

A diagram of the apparatus is shown in Fig. 1. The reactor, a 360 ml Pyrex sphere containing a Teflon stirring bar, was provided with a sidearm 2.1 cm i.d. by 4.5 cm long which was sealed with a Suprasil quartz window 0.3 cm thick. The flask was attached to a mercury-free vacuum line for filling and evacuation. Sample pressures were measured using either of two absolute dial gauges, 0 - 20 and 0 - 400 Torr respectively, which were calibrated against a Zimmerli-type mercury manometer. During calibration, a

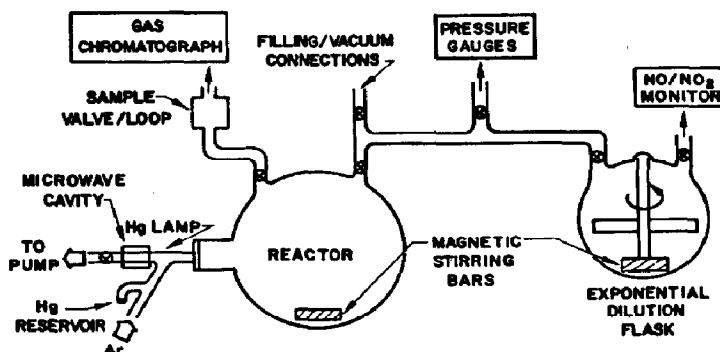


Fig. 1. Schematic diagram of the apparatus for  $O(^1D)/N_2O$  measurements.

liquid nitrogen trap was placed between the Zimmerli gauge and the dial gauges to prevent contamination of these dial gauges with mercury. Actinic radiation at 184.9 nm was provided by a low pressure glow of mercury in argon sustained by a 120 W microwave (2450 MHz) discharge source operated at 70 - 100% of maximum output. The discharge tube (0.8 cm i.d.) was attached directly to the quartz window of the reactor for maximum intensity.

From the steady state assumption for  $O(^1D)$  for reactions (1) and (2) it follows (compare, for example, WP [4]) that

$$R = \frac{k_{1a}}{k_{1b}} = \frac{[N_2]}{[NO]} - \frac{1}{2} = \frac{X_{N_2}}{X_{NO}} - \frac{1}{2} \quad (3)$$

where  $X_{N_2}$  and  $X_{NO}$  are the mole fractions of  $N_2$  and  $NO$  produced from reactions (1a) and (1b). The value of  $R$  is obtained from measurements of  $X_{N_2}$  and  $X_{NO}$  after photolysis. For  $N_2$  a gas chromatograph (g.c.) equipped with a molecular sieve 5A column operated at about 380 K was used. To facilitate sampling without accidental contamination with air, a helium-purged sampling valve with a stainless steel sample loop of volume about 10 ml was attached directly between the g.c. and the reactor. The  $NO/NO_x$  chemiluminescence analyzer operated at a sample flow rate of 3 ml (STP)  $s^{-1}$  and a reactor pressure of approximately 4 Torr. For most of this work this instrument was equipped with an  $NO_2$ -to- $NO$  converter of which the active element is Pt-Rh resistance wire maintained at 1100 K by joule heating.

The photolysis experiments were carried out on pure  $N_2O$  (30 - 130 Torr) and on  $N_2O$  (30 - 130 Torr)-He mixtures at atmospheric pressure. Experiments with and without added helium were interspersed.  $N_2O$  (minimum purity 99.9%) and helium (minimum purity 99.995%) were used without further purification. The photolyses were carried out for periods ranging from 30 to 120 min with continuous stirring, with an additional 10 min of post-experimental stirring to ensure thorough mixing. Part of the photolyzed mixture was then expanded into the g.c. sampling loop for  $X_{N_2}$  measurement and the remainder was used for  $NO_x$  analysis.

To determine  $X_{N_2}$  the content of the sampling loop was injected into the g.c. The g.c. was calibrated with a standard mixture of  $N_2$  (5.22%) in

helium using the same technique as in sample analysis, *i.e.* the calibration gas was introduced into the reactor and transferred to the g.c. in the same manner as the photolyzed mixture. The g.c. response at a number of reactor pressures  $P_r$  was measured and plotted against  $P_r X_{N_2}$ . Using this calibration plot, the g.c. response from the photolyzed mixtures was determined. To ascertain that no systematic errors resulted in the analysis owing to the presence of helium, in one undiluted  $N_2O$  experiment the reactor was brought to atmospheric pressure with helium before  $N_2$  and  $NO$  analysis.

For determination of  $X_{NO}$  a portion of the photolyzed mixture, containing about 5 - 10 Torr  $N_2O$ , was admitted to the 2 l exponential dilution flask (Fig. 1) where it was brought to atmospheric pressure with  $N_2$ . After stirring for 10 min the flask was connected to the  $NO/NO_x$  monitor.  $NO/NO_x$  measurements were made over dilution periods of about 16 min.  $N_2$  was used as dilution gas and stirring was continuous.  $NO$  and  $NO_x$  were monitored alternately for periods of about 4 min each. Plots of these measurements,  $NO(NO_x)$  versus time, were then extrapolated to  $t = 0$  to determine the  $[NO]$  and  $[NO_x]$  (and hence by subtraction also  $[NO_2]$ ) originally present in the dilution flask. From a knowledge of the original pressure of the undiluted sample in the dilution flask, the mole fractions  $X'_{NO}$  and  $X'_{NO_2}$  in the photolyzed mixture were obtained. Since the  $NO_2$  is the result of oxidation of  $NO$  by  $O_2$  formed during the photolysis, the sum of these quantities is the  $X_{NO}$  to be used in eqn. (3). In some experiments a second sample was admitted from the reactor into the dilution flask for analysis; the resulting  $X_{NO}$  was found to agree within experimental error with those of the first determination. The calibration of the monitor was checked before and after each photolysis experiment with a standard mixture of  $96 \pm 2$  ppm  $NO$  in  $N_2$ .

A complicating factor in these  $NO_x$  measurements was the presence of  $N_2O$ . The low flow Pt-Rh catalytic  $NO_2$ -to- $NO$  converter [9] used in most of this work is normally heated resistively to about 1300 K at which temperature 99% of the  $NO_2$  is converted to  $NO$ . At this temperature up to 1% of the  $N_2O$  is also converted to  $NO$ . Because of the large excess of  $N_2O$  in the photolyzed mixture, such high  $N_2O$  conversion was unacceptable in the present work. However, by reducing the temperature of the converter to about 1100 K, the  $N_2O$  conversion was reduced to an acceptable level (0.01 - 0.08%), for which reasonable corrections could be made. Under these conditions the  $NO_2$ -to- $NO$  conversion efficiency was  $75 \pm 15\%$ . In attempts to use a stainless steel converter [9] at about 1100 K, it was found that while  $N_2O$  conversion was again minimal, the response of this converter is highly erratic under these conditions and therefore it was not used. Chemical converters [9] operate at lower temperatures and do not convert  $N_2O$ . In some experiments a Mohr's salt ( $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ ) converter at room temperature [13, 14] was therefore used; no measurable  $N_2O$  conversion occurred and the  $NO_2$ -to- $NO$  conversion efficiency was found to be  $90 \pm 10\%$ . Results obtained with the Pt-Rh and the Mohr's salt converters are in good agreement (see later).

## 2.2. Correction factors and error analysis

The data were analyzed in two groups (photolyses of "pure" NO<sub>2</sub> and N<sub>2</sub>O diluted in helium) using a propagation of errors treatment for random errors [15]. Each experimental value of  $R_i$  was subjected to this treatment and an uncertainty  $\sigma_i$  due to random errors was obtained. The values of  $\sigma_i$  were used to obtain a weighted average of  $\bar{R}$  according to [16]

$$\bar{R} = \frac{\sum_i (R_i / \sigma_i^2)}{\sum_i (1 / \sigma_i^2)}$$

The standard deviation  $\sigma$  in the mean was obtained from

$$\sigma = \left\{ \frac{1}{\sum_i (1 / \sigma_i^2)} \right\}^{1/2}$$

Estimated systematic errors were summed for each experiment and the average of these was added to  $\sigma$  to obtain an estimate of the absolute accuracy.

A number of correction factors had to be applied to the raw data. These are discussed here with the associated random and systematic errors.

### 2.2.1. Random errors

(1) A small difference in response was observed between measurements of the same "NO<sub>2</sub>-free" NO samples in the NO and NO<sub>x</sub> modes of the chemiluminescence analyzer. The "NO<sub>x</sub>" mode yielded consistently lower readings than the "NO" mode, by  $2 \pm 1\%$  with the Pt-Rh converter and by  $3.5 \pm 1\%$  with the Mohr's salt converter. These differences are apparently related to a small decrease in sample flow in the NO<sub>x</sub> mode and the NO<sub>x</sub> measurements obtained were corrected for this effect.

(2) The random error in extrapolating the NO/NO<sub>x</sub> exponential dilution plots back to  $t = 0$  is estimated not to exceed  $\pm 1\%$ .

(3) For experiments with the Pt-Rh converter a correction had to be applied for N<sub>2</sub>O conversion to NO. Because of variations in the efficiency of this process, which is strongly temperature dependent, the magnitude of the correction needed was frequently checked. In most of the work this correction was 0.08% resulting, in the worst case, in having to subtract 7.8% from the NO<sub>x</sub> reading. We estimate the error in this procedure to be no more than 50% of the correction factor; this thus introduces a maximum random uncertainty of  $\pm 3.9\%$  in  $X_{\text{NO}}$ . When the Mohr's salt converter was used, of course, no such error was involved.

(4) [NO<sub>2</sub>] in the photolyzed mixtures was in the range 0 - 15% of total [NO<sub>x</sub>]. As discussed in Section 2.1 the Pt-Rh converter operated at an NO<sub>2</sub>-to-NO conversion efficiency of  $75 \pm 15\%$  and the Mohr's salt converter at  $90 \pm 10\%$ . The maximum random error in  $X_{\text{NO}}$  due to uncertainties in the NO<sub>2</sub> conversion efficiency is  $\pm 2.25\%$  for the Pt-Rh converter and  $\pm 1.5\%$  using the Mohr's salt converter.

(5) Errors resulting from reading the dial pressure gauges are estimated to be a maximum of  $\pm 2\%$  over the pressure range measured in these experiments for both the N<sub>2</sub> and NO determinations.

(6) The error in individual gas chromatographic determinations of  $N_2$  from the photolysis mixture was obtained from the scatter in the calibration data as  $\pm 7.2\%$  in the undiluted  $N_2O$  samples and  $\pm 2.5\%$  in the  $N_2O$  samples diluted with helium.

### 2.2.2. Systematic errors

Systematic errors arise because of uncertainties in concentrations of  $N_2$  and  $NO$  in the two calibration mixtures, uncertainties in the calibration of pressure gauges and uncertainties in the determination of the various correction factors.

(1) The uncertainty in the concentration of  $NO$  in the calibration sample is estimated to be no more than 2%.

(2) The calibration gas obtained from the Matheson Co. was analyzed by the manufacturer to be 5.22%  $N_2$  in helium with an accuracy of 2% of the  $N_2$  content. A second analysis on this gas cylinder performed at M.G. Scientific yielded 5.23% with an accuracy of 1%; because of the good agreement the latter was used as the accuracy figure.

(3) From the dial pressure gauge calibration against the Zimmerli gauge, the absolute pressure is accurately known to  $\pm 0.3\%$  in the range of the present measurements.

(4) The systematic error in the g.c. calibration was taken to be numerically equal to the standard deviation of the calibration measurements, *i.e.* 1.8% for undiluted  $N_2O$  measurements and 1.2% for the  $N_2O$ -He mixtures.

(5) The  $N_2O$  interference resulting from the use of the Pt-Rh converter was taken to be 25% of its value as a systematic error. This is one-half the uncertainty of a given measurement (four such interference determinations were made). No such error contribution is present for the Mohr's salt converter measurements.

(6) A 4% systematic error was taken for the  $NO_x$  converter efficiency. This reflects the  $\pm 15\%$  uncertainty of an individual measurement improved by the relatively large number (about 15) of such efficiency measurements which were made. For the Mohr's salt converter the same uncertainty was taken since fewer efficiency measurements were made and this converter has not been as well investigated as the Pt-Rh converter. In either case the systematic error contribution is no more than 0.1%.

The total systematic error is obtained by addition of these error estimates; it is conservative since it is unlikely that all these errors will be in the same direction.

## 3. Results

The results obtained are summarized in Table 1. Within each group the  $R$  values,  $R_O$  and  $R_{He}$ , respectively, may be seen to be independent of  $[N_2O]$ , of irradiation time, of whether a Mohr's salt or Pt-Rh converter was used in the  $X_{NO}$  determination and, for the undiluted  $N_2O$  experiments, of whether the photolyzed sample was brought to atmospheric pressure with helium in

TABLE 1

Summary of  $R = k_{1a}/k_{1b}$  measurements

| [He]<br>(Torr) <sup>a</sup>                                       | [N <sub>2</sub> O]<br>(Torr) | $\Delta t_{\text{irr}}$<br>(min) | $X_{\text{N}_2}$ | $X_{\text{NO}}$ | $R_i$             | $\sigma_i$                  | Systematic<br>error in $R_i$ |
|---|------------------------------|----------------------------------|------------------|-----------------|-------------------|-----------------------------|------------------------------|
| 0   | 28.8                         | 129                              | 0.0670           | 0.0527          | 0.77              | 0.10 <sub>2</sub>           | 0.08 <sub>2</sub>            |
| 0   | 54.2                         | 60                               | 0.0299           | 0.0243          | 0.73 <sup>b</sup> | 0.09 <sub>3</sub>           | 0.08 <sub>4</sub>            |
| 0   | 100.0                        | 57                               | 0.0240           | 0.0193          | 0.74              | 0.07 <sub>3</sub>           | 0.09 <sub>0</sub>            |
| 0   | 116.5                        | 50                               | 0.0185           | 0.0151          | 0.72 <sup>c</sup> | 0.09 <sub>3</sub>           | 0.06 <sub>6</sub>            |
| 0   | 128.5                        | 30                               | 0.0072           | 0.0059          | 0.72              | 0.09 <sub>8</sub>           | 0.07 <sub>2</sub>            |
| 0   | 128.5                        | 60                               | 0.0130           | 0.0107          | 0.71              | 0.09 <sub>3</sub>           | 0.07 <sub>1</sub>            |
| Weighted mean, standard deviation and average<br>systematic error |                              |                                  |                  |                 | 0.73 <sub>4</sub> | 0.03 <sub>7</sub><br>(5.0%) | 0.07 <sub>8</sub><br>(10.6%) |
| $\bar{R}_0$ and its estimated accuracy                            |                              |                                  |                  |                 | 0.73 <sub>4</sub> | $\pm 0.11_3$                |                              |
| 648.0   | 29.1                         | 50                               | 0.00115          | 0.00079         | 0.95 <sup>c</sup> | 0.09 <sub>6</sub>           | 0.06 <sub>9</sub>            |
| 730.4   | 29.5                         | 110                              | 0.00255          | 0.00193         | 0.82              | 0.07 <sub>4</sub>           | 0.07 <sub>0</sub>            |
| 724.0   | 34.0                         | 81                               | 0.00188          | 0.00132         | 0.93              | 0.08 <sub>5</sub>           | 0.07 <sub>5</sub>            |
| 725.0   | 35.5                         | 86                               | 0.00176          | 0.00134         | 0.81              | 0.07 <sub>7</sub>           | 0.07 <sub>0</sub>            |
| 719.5   | 40.5                         | 93                               | 0.00196          | 0.00152         | 0.79              | 0.07 <sub>2</sub>           | 0.06 <sub>9</sub>            |
| 628.0   | 51.5                         | 60                               | 0.00211          | 0.00142         | 0.99 <sup>c</sup> | 0.06 <sub>7</sub>           | 0.07 <sub>1</sub>            |
| 622.1   | 66.0                         | 90                               | 0.00246          | 0.00162         | 1.00 <sup>c</sup> | 0.06 <sub>0</sub>           | 0.07 <sub>2</sub>            |
| 669.8   | 73.5                         | 45                               | 0.00154          | 0.00102         | 1.04              | 0.07 <sub>2</sub>           | 0.10 <sub>7</sub>            |
| 688.0   | 75.5                         | 45                               | 0.00191          | 0.00139         | 0.87              | 0.04 <sub>5</sub>           | 0.08 <sub>9</sub>            |
| 668.0   | 97.0                         | 49                               | 0.00280          | 0.00181         | 1.04              | 0.08 <sub>0</sub>           | 0.10 <sub>6</sub>            |
| Weighted mean, standard deviation and average<br>systematic error |                              |                                  |                  |                 | 0.91 <sub>9</sub> | 0.02 <sub>2</sub><br>(2.4%) | 0.08 <sub>0</sub><br>(8.7%)  |
| $\bar{R}_{\text{He}}$ and its estimated accuracy                  |                              |                                  |                  |                 | 0.91 <sub>9</sub> | $\pm 0.10_0$                |                              |

<sup>a</sup> 1 Torr = 133.3 Pa =  $3.33 \times 10^{16}$  particles ml<sup>-1</sup> at 290 K.<sup>b</sup> Photolysis mixture brought to atmospheric pressure with helium before analysis; in all other experiments with undiluted N<sub>2</sub>O the samples were transferred directly at low pressure.<sup>c</sup> [NO<sub>x</sub>] analysis used Mohr's salt converter; in all other experiments the Pt-Rh converter was used.

the reactor or was transferred to the g.c. and the dilution flask at reaction pressure.

Since all the systematic errors, except for the g.c. calibration, are the same for the experiments with and without helium, the difference between these two groups should be judged by the random errors in the respective ratios plus the  $\pm 1.2\%$  and  $\pm 1.8\%$  uncertainty in the g.c. calibrations for these two sets of experiments, respectively. Calculated this way  $R_0 = 0.73_4 \pm 0.05_9$  and  $R_{\text{He}} = 0.91_9 \pm 0.03_9$ . Their ratio  $0.79_9 \pm 0.09_8$  is indicative of a definite influence of the presence of helium.

Summing all the estimated systematic errors with  $\sigma$  yields

$$\bar{R}_0 = 0.73_4 \pm 0.11_3 \quad \bar{R}_{\text{He}} = 0.91_9 \pm 0.10_0$$

#### 4. Discussion and conclusions

The value determined for  $\bar{R}_0$  ( $0.73 \pm 0.11$ ) is in good agreement with those of Heicklen *et al.* [7] ( $0.65 \pm 0.10$ ), Davidson *et al.* [12] ( $0.68 \pm 0.11$ ) and Ghormley *et al.* [6] ( $0.70$ ). The error figures quoted pertain to reasonable estimates of accuracy, as given in their papers. The experimental conditions of ref. 6, however, are not clearly defined, and so a dependable accuracy estimate does not seem possible. The mean value of WP [4] ( $R_0 = 0.97$ ) is further removed but that  $R$  value and the present one lie within the combined error limits of  $0.17$  (WP) +  $0.11$  (present work)<sup>†</sup> =  $0.28$ . One difference from the present experiment is that WP used continuum radiation from a flashlamp and photolyzed  $N_2O$  over the 185 - 230 nm region. However, the radiation intensity from such lamps increases by about a factor of 3 over this range toward the long wavelength end [17], while the photodissociation cross section decreases by a factor of  $10^3$  in the same direction [18]. This suggests that most  $O(^1D)$  was produced with energies close to those of the present work. Moreover, since Heicklen *et al.* [7] did not see an influence on  $R$  in either undiluted  $N_2O$  photolysis or  $N_2O$ -He photolysis between 184.9 and 213.9 nm radiation, this is an unlikely explanation for the apparent variation in  $R_0$ .  $R_0 = 0.8 \pm 0.1$  would be within the error limits of all the determinations and it would be an optimistic assessment of the accuracy of the various results now available to attribute physical significance to the different mean values.

Consider now our  $\bar{R}_{He} = 0.92 \pm 0.10$ . This result is in agreement with the sets of results of Heicklen [7] ( $0.83 \pm 0.10$ ), Davidson *et al.* [12] ( $0.79 \pm 0.13$ ) and WP [4] ( $1.00 \pm 0.17$ ). Therefore, we concur with Heicklen's [7] recommendation, based on an assessment of the then available literature, of  $R = 0.9 \pm 0.1$  for thermally modified  $O(^1D)$ . Such  $O(^1D)$  probably compares more closely than does hot  $O(^1D)$  to that reacting in the stratosphere, considering that only about one collision in ten with  $N_2$  and  $O_2$ , the major "bath" compounds present, leads to  $O(^1D)$  electronic quenching [19].

It remains somewhat mystifying that the Ottawa workers [4, 5] find no evidence for an influence of helium on  $R$ . Neither did WP observe an effect of added neon. However, their error limits do not exclude such effects. The present  $R_0/R_{He} = 0.80 \pm 0.10$  may be compared with that which can be calculated from the other works, using the sum of the percentage standard deviations of the  $R_0$  and  $R_{He}$  measurements to arrive at the uncertainty limits, *i.e.*  $R_0/R_{He}$  of  $0.97 \pm 0.24$  for WP [4],  $0.85 \pm 0.08$  for Davidson *et al.* [12] and  $0.78 \pm 0.14$  for Heicklen [7]. Preston's work [5] contains only one helium-modified measurement, which measurement allows the rough estimate  $\bar{R}_0/R_{He} = 1.17 \pm 0.4$ , where the error limit is taken to be double that for their pure  $N_2O$  photolysis experiments. All of these values overlap within the

<sup>†</sup>The most reliable [7] value of the set of measurements made by Preston *et al.* [5] ( $R = 1.01$  with a standard deviation of  $0.06$ ) pertains to  $O(^1D)$  from  $NO_2$  photolysis under conditions leading to little excess energy and probably compares better with the kinetically modified results discussed in the next paragraph.



stated error limits and we conclude that the helium-induced kinetic energy modification effect is real. The existence of this effect is also qualitatively consistent with the existence of a temperature dependence of  $R_{\text{He}}$ , discussed by Davidson *et al.* [12].

## Acknowledgments

This work was supported in part by the Transportation Systems Center for the High Altitude Program of the Federal Aviation Administration, U.S. Department of Transportation, under contract DOT-TSC-1200. We thank Dr. G. Paraskevopoulos for helpful correspondence.

## References

- 1 A. J. Grobecker (ed.), *Department of Transportation, The Natural Stratosphere of 1974, CIAP Monograph 1, DOT-TST-75-51, NTIS PB 246 318*, September 1975.
- 2 J. A. Davidson, H. I. Schiff, G. E. Streit, J. R. McAfee, A. L. Schmeltekopf and C. J. Howard, *J. Chem. Phys.*, **67** (1977) 5021.
- 3 G. Paraskevopoulos, V. B. Symonds and R. J. Cvetanovic, *Can. J. Chem.*, **50** (1972) 1808.
- 4 H. A. Wiebe and G. Paraskevopoulos, *Can. J. Chem.*, **52** (1974) 2165.
- 5 P. M. Scott, K. F. Preston, R. J. Andersen and L. M. Quick, *Can. J. Chem.*, **49** (1971) 1808.
- 6 J. A. Ghormley, R. L. Ellsworth and C. J. Hochenadel, *J. Phys. Chem.*, **77** (1973) 1341.
- 7 R. Simonaitis, R. I. Greenberg and J. Heicklen, *Int. J. Chem. Kinet.*, **4** (1972) 497.
- 8 R. Overend, G. Paraskevopoulos, J. R. Crawford and H. A. Wiebe, *Can. J. Chem.*, **53** (1975) 1915.
- 9 A. Fontijn, in E. L. Wehry (ed.), *Modern Fluorescence Spectroscopy: Newer Techniques and Applications*, Vol. 1, Plenum Press, New York, 1976, p. 159.
- 10 A. Fontijn, A. J. Sabadell and R. J. Ronco, *Anal. Chem.*, **42** (1970) 575.
- 11 *U.S. Department of Transportation and NASA Upper Atmospheric Programs Bulletin 77-5*, 1977, and R. J. Pirkle, H. N. Volltrauer, W. Felder and A. Fontijn, *Final Report FAA-AEQ-77-10*, 1977.
- 12 J. A. Davidson, C. J. Howard, H. I. Schiff and F. C. Fehsenfeld, *J. Chem. Phys.*, **70** (1979) 1697.
- 13 T. W. Winfield, *Am. Chem. Soc., Div. Environmental Chem., Prepr.*, **17** (1977) 372.
- 14 W. A. McClenny and R. K. Stevens, EPA, NERC, personal communication to A. Fontijn, April 1977.
- 15 R. J. Cvetanovic, R. P. Overend and G. Paraskevopoulos, *Int. J. Chem. Kinet., Symp.* **1** (1975) 249.
- 16 P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, 1969, Chap. 5.
- 17 J. R. McNesby, W. Braun and J. Ball, in A. A. Lamola (ed.), *Creation and Detection of the Excited State*, Vol. 1, Part B, Marcel Dekker, New York, 1971, p. 503.
- 18 D. R. Bates and P. B. Hays, *Planet. Space Sci.*, **15** (1967) 189.
- 19 G. E. Streit, C. J. Howard, A. L. Schmeltekopf, J. A. Davidson and H. I. Schiff, *J. Chem. Phys.*, **65** (1976) 4761.