

# Temperature-dependent quantum yields for O(<sup>3</sup>P) and O(<sup>1</sup>D) production from photolysis of O<sub>3</sub> at 248 nm

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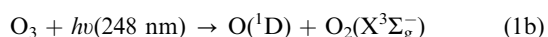
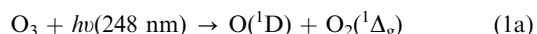
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Received 17th September 2004, Accepted 19th October 2004  
First published as an Advance Article on the web 5th November 2004

A pulsed laser photolysis–resonance fluorescence technique was employed independently by two laboratories to measure  $\Phi_{\text{O}_3\text{P}}$ , the quantum yield for production of O(<sup>3</sup>P) from O<sub>3</sub> photolysis at 248 nm, between 196 and 427 K. The agreement between the two studies is very good, and the combined results are adequately represented by the function  $\Phi_{\text{O}_3\text{P}} = (0.115 \pm 0.030) \times \exp((35 \pm 60)/T)$  where the uncertainties are  $2\sigma$ . Within experimental uncertainties, the new results are in agreement with previously reported room temperature results as well as with the single previous temperature dependence study, and greatly reduce the uncertainties in  $\Phi_{\text{O}_3\text{P}}(T)$  and  $\Phi_{\text{O}_1\text{D}}(T)$  ( $=1 - \Phi_{\text{O}_3\text{P}}(T)$ ) especially at temperatures other than room temperature. The yield of O(<sup>3</sup>P) in the reaction of O(<sup>1</sup>D) with O<sub>3</sub> is shown to be greater than unity at room temperature and below, and to increase slightly with decreasing temperature.

## Introduction

The photochemistry of ozone (O<sub>3</sub>) in the UV region has been studied extensively. Interest in O<sub>3</sub> photochemistry centers on its importance in atmospheric chemistry,<sup>1</sup> although it has also been studied extensively by both experimental<sup>2–11</sup> and theoretical<sup>12–14</sup> groups whose primary interest has been characterization of the photo-dissociation dynamics. Because only radiation at wavelengths longer than 290 nm penetrates into the lower atmosphere, and because O(<sup>1</sup>D) is the photo-fragment of primary atmospheric importance,<sup>1</sup> an enormous effort has focused on establishing the wavelength and temperature dependence of the O(<sup>1</sup>D) quantum yield at  $\lambda > 290$  nm. It now appears that both spin-allowed and spin-forbidden pathways are operative in producing O(<sup>1</sup>D):



The complete data base has recently been critically reviewed, and a set of recommended values for the O(<sup>1</sup>D) quantum yield,  $\Phi_{\text{O}_1\text{D}}(\lambda, T)$ , has been proposed.<sup>15</sup>

Quantum yields for O(<sup>1</sup>D) production from O<sub>3</sub> photolysis in the wavelength range 220–290 nm have also been reported in a number of studies.<sup>2,3,6,16–25</sup> With the exception of the earliest study,<sup>16</sup> which has been superseded by subsequent work from the same group,<sup>17</sup> reported values for  $\Phi_{\text{O}_1\text{D}}(\lambda)$  at room temperature are in the range 0.83 to 0.94 with little or no wavelength dependence. A table summarizing the measured

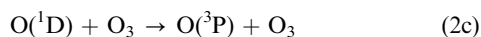
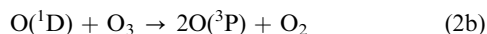
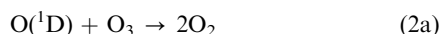
room temperature quantum yields, the species monitored to obtain the quantum yield data, and the reference wavelengths and assumed quantum yields employed in studies where the absolute quantum yields were not measured directly is published elsewhere.<sup>25</sup>

In a number of the studies cited above, the directly measured species was the ground state oxygen atom, O(<sup>3</sup>P). In these studies, the quantum yield ratio  $\Phi_{\text{O}_3\text{P}}/\Phi_{\text{O}_1\text{D}}$  is evaluated by comparing the O(<sup>3</sup>P) signal obtained directly from photolysis to that obtained when all O(<sup>1</sup>D) is deactivated to O(<sup>3</sup>P) by a non-reactive quencher; the quantum yields are put on an absolute scale by applying the (certainly valid) assumption that, at wavelengths longer than 220 nm,  $\Phi_{\text{O}_1\text{D}} + \Phi_{\text{O}_3\text{P}} = 1.00$  or very close to unity.

A number of the published studies of O<sub>3</sub> photochemistry in the 220–290 nm wavelength range report values for  $\Phi_{\text{O}_3\text{P}}$  at the excimer laser wavelength 248 nm. The reported room temperature values for  $\Phi_{\text{O}_3\text{P}}$  are  $0.01 \pm 0.01$ ,<sup>16</sup>  $0.15 \pm 0.02$ ,<sup>17</sup>  $0.093 \pm 0.028$ ,<sup>19</sup>  $0.06 \pm 0.01$ ,<sup>20</sup>  $0.10 \pm 0.05$ ,<sup>24</sup> and  $0.086 \pm 0.019$ .<sup>25</sup> As mentioned above, the earliest reported value<sup>16</sup> is thought to be in error because of problems with the detector response time.<sup>17</sup>

Only a single study of the temperature dependence of O<sub>3</sub> photolysis quantum yields in the 220–290 nm wavelength range has been reported. Talukdar *et al.*<sup>24</sup> coupled time-resolved detection of O(<sup>3</sup>P) by atomic resonance fluorescence spectroscopy with 248 nm laser flash photolysis of O<sub>3</sub>/He mixtures to obtain values for  $\Phi_{\text{O}_3\text{P}}(T)$  at eight temperatures ranging from 201 K to 319 K; a temperature-independent quantum yield of  $0.09 \pm 0.06$  was reported.<sup>24</sup> The data analysis in the Talukdar

*et al.*<sup>24</sup> study requires that the overall yield of O(<sup>3</sup>P) from the O(<sup>1</sup>D) + O<sub>3</sub> reaction be known.

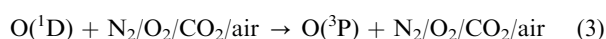
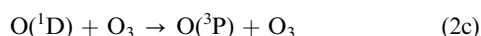
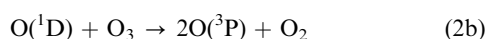
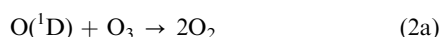
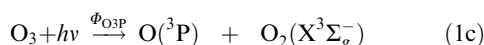
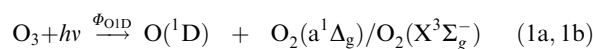


The available literature suggests that the O(<sup>3</sup>P) yield from reaction (2) is 1.0,<sup>16,24,26</sup> although the uncertainty in this yield appears to be significant.

The two research groups collaborating in this work have recently published papers describing measurements of temperature-dependent rate coefficients for O(<sup>1</sup>D) reactions with a variety of collision partners, several of which deactivate O(<sup>1</sup>D) to O(<sup>3</sup>P) with essentially unit yield;<sup>27,28</sup> in those studies, 248 nm laser flash photolysis of O<sub>3</sub> was employed as the O(<sup>1</sup>D) source. The extensive data sets employed to obtain the kinetic data<sup>27,28</sup> can also be analyzed to obtain values for  $\Phi_{\text{O}(\text{P})}(T)$ , and these results are reported in this paper. The new results greatly expand the study of Talukdar *et al.*<sup>24</sup> by covering a wider temperature range (197–427 K) and employing a number of non-reactive collision partners. The new results can also be used to evaluate the temperature dependence of the O(<sup>3</sup>P) yield from reaction (2), thereby examining the possibility that the temperature-dependent quantum yields reported by Talukdar *et al.*<sup>24</sup> may have a small error because their data analysis assumed unit yield of O(<sup>3</sup>P) from reaction (2) and that this yield did not change with temperature.

## Experimental method

During the above mentioned kinetic studies,<sup>27,28</sup> temporal profiles of O(<sup>3</sup>P) were recorded following the 248 nm photolysis of O<sub>3</sub>. In the presence of a collision partner (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> or air), the following reactions take place:



O(<sup>1</sup>D) → Loss by reaction with background impurities, and by diffusion from the detector field of view (4)

O(<sup>3</sup>P) → Loss by reaction with O<sub>3</sub> and background impurities, and by diffusion from the detector field of view (5)

The quencher in reaction (3) simply depends on which collision partner was being studied. The temporal profiles obtained under these conditions are described by a biexponential equation:

$$[\text{O}(\text{P})]_t = Ae^{-Bt} + Ce^{-Dt} \quad (I)$$

In eqn. (I),  $A$ – $D$  are given by the following (using N<sub>2</sub> as the example):

$$A = \gamma[\text{O}(\text{D})]_0 \frac{(k_2\theta_2 [\text{O}_3] + k_3\theta_3 [\text{N}_2])}{(D - B)} \quad (II)$$

$$B = k_2 [\text{O}_3] + k_3 [\text{N}_2] + k_4 \quad (III)$$

$$C = S_0 - A \quad (IV)$$

$$D = k_5 \quad (V)$$

In eqn. (II),  $\theta_2$  and  $\theta_3$  are the number of O(<sup>3</sup>P) atoms produced per atom of O(<sup>1</sup>D) that reacts with O<sub>3</sub> or is quenched

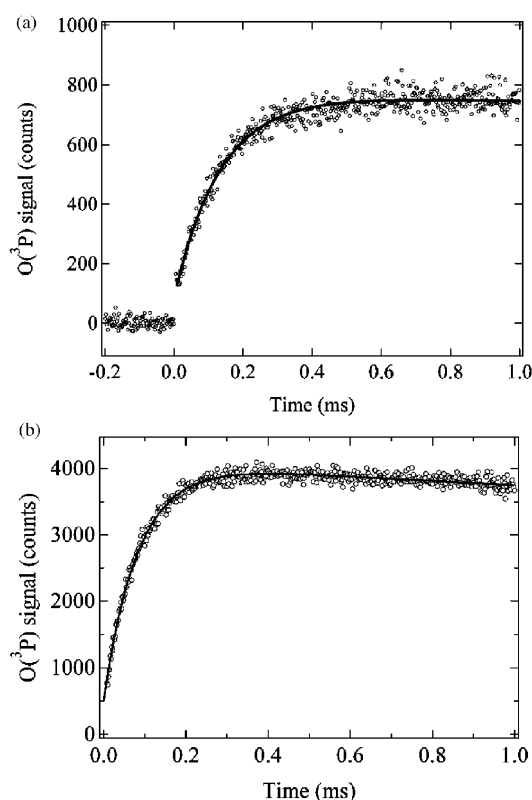
by a collision partner, respectively;  $\gamma$  is a parameter that relates the resonance fluorescence signal to the O(<sup>3</sup>P) concentration, *i.e.*,  $\gamma[\text{O}(\text{D})]_0$  is the signal that would result from conversion of O(<sup>1</sup>D) to O(<sup>3</sup>P) with unit yield. In eqn. (IV),  $S_0$  is the resonance fluorescence signal immediately after the 248 nm photolysis flash ( $S_0 \equiv \gamma[\text{O}(\text{P})]_0$ ). We note that these collision partners quench/remove O(<sup>1</sup>D) very rapidly and any impurities in them contribute negligibly to the removal of O(<sup>1</sup>D); this contribution is at most 1%.

Each individual yield measurement involved recording 5–12 temporal profiles of O(<sup>3</sup>P) in the presence of varying concentrations of the collision partner. Typical measured temporal profiles and the associated best fits to eqn. (I) are shown in Fig. 1 for the NOAA and Georgia Tech. groups. To evaluate the desired quantum yield, we first define the parameter  $\beta$  to be the ratio of O(<sup>3</sup>P) produced by photolysis to that produced by O(<sup>1</sup>D) deactivation. In terms of the parameters evaluated by fitting the observed O(<sup>3</sup>P) temporal profiles to eqn. (I),

$$\beta = \frac{B(C + A)}{A(D - B)} \quad (VI)$$

When the quencher deactivates O(<sup>1</sup>D) to O(<sup>3</sup>P) with unit yield, then the following relationship holds:<sup>29,30</sup>

$$\frac{B}{\beta} = \frac{1}{\beta^*} (B - B_0) + \frac{B_0}{\beta_0} \quad (VII)$$



**Fig. 1** Typical O(<sup>3</sup>P) temporal profiles following O<sub>3</sub> photolysis at 248 nm in the presence of a reactant or quencher of O(<sup>1</sup>D) observed at (A) NOAA and (B) Georgia Tech. The photolysis laser fired at time = 0. (a) NOAA experimental conditions:  $T = 295$  K;  $P = 48$  Torr He; added quencher: N<sub>2</sub>; concentrations:  $[\text{O}_3] = 1.4 \times 10^{13}$  per cm<sup>3</sup>;  $[\text{O}]_0 \sim 9 \times 10^{11}$  per cm<sup>3</sup>;  $[\text{N}_2] = 5.69 \times 10^{13}$  per cm<sup>3</sup>. The solid line is the best fit of the data to eqn. (I). The best fit parameters are  $A = -683 \pm 16$ ,  $B = 7491 \pm 292$  s<sup>-1</sup>,  $C = 767 \pm 4$ ,  $D = 27.4 \pm 2.6$  s<sup>-1</sup>; uncertainties are  $2\sigma$ , precision only. (b) Georgia Tech experimental conditions:  $T = 221$  K;  $P = 20$  Torr He; added quencher: N<sub>2</sub>; concentrations:  $[\text{O}_3] = 1.7 \times 10^{12}$  per cm<sup>3</sup>;  $[\text{O}]_0 \sim 6 \times 10^{11}$  per cm<sup>3</sup>;  $[\text{N}_2] = 2.77 \times 10^{14}$  per cm<sup>3</sup>. The solid line is the best fit of the data to eqn. (I). The best fit parameters are  $A = -3571 \pm 54$ ,  $B = 12\,005 \pm 316$  s<sup>-1</sup>,  $C = 4078 \pm 19$ ,  $D = 86.4 \pm 4.8$  s<sup>-1</sup>; uncertainties are  $2\sigma$ , precision only.

In eqn. (VII),  $\beta_0$  and  $B_0$  are the values of  $\beta$  and  $B$  observed at zero quencher concentration, and  $\beta^*$  is the value of  $\beta$  in the limit where  $O(^1D)$  is converted to  $O(^3P)$  with unit yield. According to eqn. (VII), a plot of  $B/\beta$  vs.  $(B - B_0)$  is linear and has a slope of  $1/\beta^*$ . Once  $\beta^*$  is known, the desired  $O(^3P)$  quantum yield can be obtained from the relationship

$$\Phi_{O^3P} = \frac{\beta^*}{(1 + \beta^*)} \quad (\text{VIII})$$

Typical plots of  $B/\beta$  versus  $(B - B_0)$  are shown in Fig. 2 for both the NOAA and Georgia Tech groups. The measured values of the yield of  $O(^3P)$  from  $O_3$  photolysis at 248 nm at various temperatures from the NOAA and GT groups are listed in Tables 1 and 2, respectively, along with important experimental parameters.

## Results and discussion

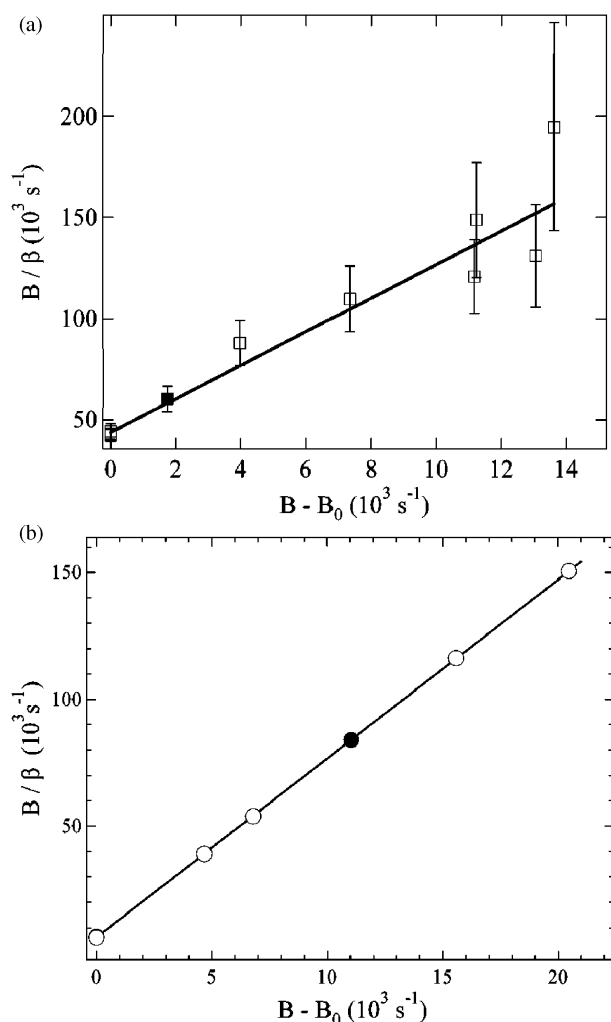
Analysis of systematic uncertainties associated with these  $O(^3P)$  yield measurements from  $O_3$  photolysis requires consideration of several issues: (1) possible contributions from removal of  $O(^1D)$  by other products that do not produce  $O(^3P)$ ,

(2) secondary production of  $O(^3P)$ , (3) uncertainties in the measurement of the concentration of  $O_3$  and the other compounds and (4) uncertainties inherent in the fitting routine. For the first issue, the most likely reaction to produce  $O(^3P)$  with a yield different from unity is the reaction of  $O(^1D)$  with  $O_3$  (reaction (2)), and that yield is reported in the literature to be 1.0 with uncertainties of  $\leq 10\%$  (Amimoto *et al.*<sup>16</sup> report  $\Theta_2 = 1.01 \pm 0.05$ , Davenport *et al.*<sup>26</sup> report  $\Theta_2 = 1.00 \pm 0.08$ , and Talukdar *et al.*<sup>24</sup> report  $\Theta_2 = 1.0 \pm 0.1$ ). We discuss the  $O(^3P)$  yield from  $O(^1D) + O_3$  in more detail below. The  $O(^1D) + N_2$  reaction is known to have an addition channel, but it is well-established that the branching ratio for addition is less than  $10^{-6}$  at the pressures and temperatures employed in this study.<sup>31</sup> Spin allowed production of  $CO + O_2(^1\Delta)$  from the  $O(^1D) + CO_2$  reaction is energetically feasible, but the  $O(^3P)$  yield is reported to be  $0.99 \pm 0.03$ ;<sup>32</sup> the negligible yield of  $CO + O_2$  has been rationalized on theoretical grounds by Wiesenfeld.<sup>33</sup> For the second issue, the most likely mechanism for the secondary production of  $O(^3P)$  is the quenching of  $O(^1D)$  by  $O_2$  to produce  $O_2(^1\Sigma_g^+)$  followed by the reaction of  $O_2(^1\Sigma_g^+)$  with  $O_3$  to produce  $O(^3P)$ . The concentrations of  $O_3$  were kept at a minimum for the  $O(^1D) + O_2$  quenching experiments, and the maximum amount of  $O(^3P)$  generated from this secondary pathway was estimated to be at most 5% of the total  $O(^3P)$  made from the primary quenching of  $O(^1D)$  by  $O_2$  (it was considerably less than 5% in the Georgia Tech experiments because very low ozone levels were employed (see Table 2)). For the third issue, the uncertainties in the measurement of the concentrations of  $O_3$  and the other compounds are based on the errors in the pressure ( $\pm 2\%$ ) and flow measurements ( $\pm 2\%$ ) and the absorption lamp intensity measurements for the  $O_3$  concentration determinations ( $\pm 2\%$ ), which result in a total uncertainty in the concentration measurements of  $\pm 5\%$ . For the last issue, the uncertainties inherent in the fit have been described elsewhere<sup>27</sup> and are estimated to be  $\pm 3\%$ . In summary, the systematic uncertainties result in a total uncertainty in the measured  $\Phi_{O^3P}$  of less than  $\pm 15\%$ , which we use as a conservative upper limit for our reported uncertainty.

Turning to the results for  $\Phi_{O^3P}$  from  $O_3$  photolysis at 248 nm, the calculated  $\Phi_{O^3P}$  showed no dependence on the identity of the collision partner concentration, as expected. The average result for  $\Phi_{O^3P}$  at room temperature from the NOAA group is  $(0.12 \pm 0.03)$ , and from the Georgia Tech group is  $(0.12 \pm 0.01)$ , where the uncertainties are  $2\sigma$  and represent precision only. These results are in excellent agreement with the previous studies mentioned in the Introduction as well as the current recommendation for  $\Phi_{O^3P} = (0.10 - 0.15)$ .<sup>34</sup> The results from both the NOAA and Georgia Tech groups for  $\Phi_{O^3P}$  as a function of temperature over the range 196–427 K are shown in Fig. 3. The combined data set is adequately described by the equation:

$$\Phi_{O^3P} = (0.115 \pm 0.030) \times \exp\left(\frac{(35 \pm 60)}{T}\right) \quad (\text{IX})$$

with the uncertainties reported at the  $2\sigma$  level, which incorporate both precision and systematic uncertainties (discussed above). As is evident, the temperature dependence is slight, resulting in a difference in  $\Phi_{O^3P}(T)$  from  $\Phi_{O^3P}(295 \text{ K})$  of no more than 10% at either end of the temperature range explored in this study; hence, the much larger  $\Phi_{O^1D}(T)$  changes by no more than 2% over the temperature range investigated. Therefore, previous laboratory studies employing the 248 nm photolysis of  $O_3$  at temperatures different from room temperature would only require a slight correction if room temperature yields were used to evaluate the photolytically generated concentrations of  $O(^3P)$  and  $O(^1D)$ . We note that although our results do not definitively show that the temperature dependence  $\Phi_{O^3P}(T)$  is different than zero, a small increase in  $\Phi_{O^3P}$



**Fig. 2** Typical plots of  $B/\beta$  versus  $B - B_0$  (see text for explanation). In both cases, the solid line is the best fit of the data to a straight line, uncertainties in the slope and intercept are reported at the  $2\sigma$  level and represent precision only. The fit slope represents  $1/\beta^*$  and the fit intercept is  $B_0/\beta_0$ . The filled data points are those obtained from the  $O(^3P)$  temporal profiles shown in Fig. 1. (a) For data obtained at NOAA,  $T = 295 \text{ K}$  and  $P = 48 \text{ Torr He}$  with  $N_2$  as the  $O(^1D)$  quencher: slope =  $8.280 \pm 1.876$ , intercept =  $43867 \pm 4605$ ,  $\Phi_{O^3P} = 0.108$  (b) For data obtained at Georgia Tech,  $T = 221 \text{ K}$  and  $P = 20 \text{ Torr He}$  with  $N_2$  as the  $O(^1D)$  quencher: slope =  $7.053 \pm 0.018$ , intercept =  $6130 \pm 205$ ,  $\Phi_{O^3P} = 0.124$ .

**Table 1** Experimental conditions and results for O(<sup>3</sup>P) quantum yield measurements from NOAA

Reactant	Temp./K	<i>P</i> /Torr	Flow vel./cm s <sup>-1a</sup>	[O <sub>3</sub> ] (10 <sup>13</sup> cm <sup>-3</sup> )	Fluence/mJ pulse <sup>-1</sup> cm <sup>-2b</sup>	[O( <sup>1</sup> D)] <sub>0</sub> (10 <sup>11</sup> cm <sup>-3</sup> ) <sup>c</sup>	[Reactant] (10 <sup>13</sup> cm <sup>-3</sup> )	O( <sup>3</sup> P) quantum yield <sup>d</sup>
N <sub>2</sub>	295	18.5	17.9	1.00	2.9	4.0	2.61–36.6	0.123 ± 0.009
N <sub>2</sub>	295	20	29.8	1.10	2.0	3.0	2.44–3.81	0.099 ± 0.014
N <sub>2</sub>	250	25	15.8	1.05	2.6	3.7	7.7–57.0	0.106 ± 0.018
N <sub>2</sub>	250	5.5	17.0	0.90	2.0	2.4	10.0–47.3	0.099 ± 0.012
N <sub>2</sub>	220	22	15.5	0.80	3.0	3.2	8.5–46.4	0.115 ± 0.015
N <sub>2</sub>	210	28	11.8	1.00	3.3	4.4	4.6–43.1	0.113 ± 0.018
N <sub>2</sub>	273	23	17.9	1.30	3.0	5.3	3.6–38.6	0.105 ± 0.012
N <sub>2</sub>	238	26	14.2	1.10	3.0	4.4	4.0–37.4	0.108 ± 0.012
N <sub>2</sub>	343	29	18.2	1.30	3.0	5.3	2.8–43.2	0.103 ± 0.017
N <sub>2</sub>	373	31	18.6	1.10	3.0	4.4	3.5–40.2	0.108 ± 0.012
N <sub>2</sub>	318	34	14.6	1.20	2.5	4.0	3.2–46.8	0.105 ± 0.017
N <sub>2</sub>	295	15	29.7	1.10	3.0	4.4	3.5–23.9	0.096 ± 0.009
N <sub>2</sub>	295	33	13.4	1.10	2.5	3.7	8.9–62.0	0.105 ± 0.013
N <sub>2</sub>	295	33	13.5	0.90	2.5	3.0	5.7–58.0	0.112 ± 0.013
N <sub>2</sub>	295	36	12.3	1.10	2.0	3.0	6.3–53.3	0.109 ± 0.009
N <sub>2</sub>	295	33	13.4	1.10	2.5	3.7	6.9–36.6	0.121 ± 0.022
N <sub>2</sub>	295	48	9.2	1.40	4.5	8.5	5.8–48.3	0.110 ± 0.013
N <sub>2</sub>	295	22	17.2	1.00	3.5	4.7	3.3–34.3	0.092 ± 0.030
N <sub>2</sub>	295	21	21.4	1.30	2.0–5.0	3.0–9.0	3.1–35.1	0.087 ± 0.010
N <sub>2</sub>	295	18	23.0	1.00	3.5	4.0	2.3–42.4	0.101 ± 0.012
N <sub>2</sub>	295	20	20.7	1.20	4.5	7.0	3.1–43.4	0.098 ± 0.018
N <sub>2</sub>	295	23.5	17.6	1.20	5.5	8.1	5.65–50.9	0.108 ± 0.010
N <sub>2</sub>	295	26	16.1	1.20	5.0	8.0	5.93–57.4	0.107 ± 0.014
N <sub>2</sub>	295	30	14.1	1.00	3.5	7.5	4.23–45.5	0.130 ± 0.018
N <sub>2</sub>	320	33	13.9	0.90	3.5	7.0	4.98–56.5	0.130 ± 0.011
N <sub>2</sub>	370	35	15.2	0.80	3.5	5.0	2.83–53.2	0.115 ± 0.027
N <sub>2</sub>	340	36	13.6	0.70	3	5.0	4.94–61.8	0.132 ± 0.040
N <sub>2</sub>	270	33	11.9	1.00	3	7.0	5.10–60.7	0.130 ± 0.023
N <sub>2</sub>	250	34	10.7	1.10	3.5	8.0	3.63–56.7	0.124 ± 0.028
N <sub>2</sub>	230	34.5	9.8	1.30	3.5	9.5	8.31–59.9	0.145 ± 0.027
N <sub>2</sub>	210	35	8.8	1.20	3	8.5	5.91–54.8	0.159 ± 0.033
N <sub>2</sub>	295	28	16.7	1.80	2	7.0	7.1–33.2	0.108 ± 0.013
N <sub>2</sub>	295	27	15.7	1.90	2	8.0	6.9–42.1	0.109 ± 0.013
N <sub>2</sub>	295	27	15.7	1.70	2	7.0	6.4–44.0	0.098 ± 0.012
O <sub>2</sub>	295	26	16.3	0.50	2.5–5	3.0–6.0	5.21–31.7	0.129 ± 0.016
O <sub>2</sub>	295	22	19.2	0.90	3.0	6.0	10.7–24.3	0.128 ± 0.014
O <sub>2</sub>	320	26	17.7	0.50	3.0	3.0	3.92–56.5	0.132 ± 0.025
O <sub>2</sub>	295	22	19.2	0.78	3.0	5.0	17.8–33.5	0.125 ± 0.022
O <sub>2</sub>	350	25	20.1	0.60	3.0	4.0	3.95–46.8	0.119 ± 0.020
O <sub>2</sub>	370	25	21.2	0.76	2.8	4.0	4.24–45.0	0.119 ± 0.028
O <sub>2</sub>	240	25	13.8	0.84–1.15	3	8.0	5.45–53.9	0.117 ± 0.021
O <sub>2</sub>	220	28	11.3	0.52	3.75	4.0	4.88–46.1	0.140 ± 0.032
O <sub>2</sub>	265	19	20.0	1.08	3.75	9.0	2.34–43.9	0.137 ± 0.017
CO <sub>2</sub>	295	22	22	1.35	4.3	7.7	0.70–8.79	0.092 ± 0.012
CO <sub>2</sub>	295	20	19.6	1.08	2.9	7.0	1.33–9.44	0.117 ± 0.016
CO <sub>2</sub>	260	23	15.2	1.41	2.5	8.0	1.58–9.78	0.123 ± 0.009
CO <sub>2</sub>	240	21	15.4	1.07	2.5	6.0	1.33–9.40	0.107 ± 0.019
CO <sub>2</sub>	295	25	16.2	1.25	2.9	8.0	1.75–8.14	0.122 ± 0.009
CO <sub>2</sub>	280	20	19.3	0.86	2.5	5.0	1.37–11.8	0.113 ± 0.012
CO <sub>2</sub>	220	20	15.0	1.17	2.4	6.0	1.44–12.4	0.122 ± 0.017
CO <sub>2</sub>	295	18	22.3	0.94	2.75	6.0	1.93–10.6	0.115 ± 0.015
CO <sub>2</sub>	345	20	25.8	0.61	2.9	4.0	0.84–12.5	0.102 ± 0.015
CO <sub>2</sub>	370	21	26.3	0.7	3	5.0	0.94–11.9	0.108 ± 0.017
CO <sub>2</sub>	320	17	28.1	0.74	2.9	5.0	0.78–12.1	0.106 ± 0.016
CO <sub>2</sub>	295	21	20.6	1.07	2.7	7.0	2.10–13.7	0.114 ± 0.013
CO <sub>2</sub>	257	20	19.0	1.12	2.4	6.0	1.48–12.7	0.113 ± 0.010
O <sub>3</sub>	295	22	20.0	0.96–4.96	0.9	10.0	—	0.118 ± 0.012
O <sub>3</sub>	295	18	18.0	0.09–5.92	1.2–4.0	9.6	—	0.120 ± 0.016
O <sub>3</sub>	295	20	36.5	0.55–3.48	1.6–3.8	7.5	—	0.099 ± 0.022
O <sub>3</sub>	250	22	17.7	0.64–5.26	0.5–2.0	3.5	—	0.106 ± 0.015
O <sub>3</sub>	220	19	19	0.50–6.67	0.4–1.7	6.4	—	0.110 ± 0.013
O <sub>3</sub>	210	25	14	0.33–5.56	0.5–10.4	8.6	—	0.121 ± 0.020
O <sub>3</sub>	273	21	18.5	0.71–5.27	0.8–3.8	7.0	—	0.098 ± 0.011
O <sub>3</sub>	238	24	15.5	0.70–5.11	0.8–3.1	7.0	—	0.114 ± 0.014
O <sub>3</sub>	343	30	20	0.49–7.26	0.5–10.9	7.2	—	0.088 ± 0.012
O <sub>3</sub>	373	31	19	0.80–4.93	0.8–3.0	6.1	—	0.092 ± 0.021
O <sub>3</sub>	318	33	15	0.96–5.41	2.0–2.5	5.2	—	0.098 ± 0.021
O <sub>3</sub>	295	18	25	0.62–3.91	1.5–9	8.8	—	0.089 ± 0.010

<sup>a</sup> Linear flow velocity calculated for the center of the reaction cell. <sup>b</sup> All experiments run at a repetition rate of 4 Hz. <sup>c</sup> For O<sub>3</sub> experiments, reported value is maximum calculated [O(<sup>1</sup>D)]. <sup>d</sup> Uncertainties reported at 2σ level representing precision only.

**Table 2** Experimental conditions and results for O(<sup>3</sup>P) quantum yield measurements from Georgia Tech<sup>a</sup>

Reactant	T/K	[O <sub>3</sub> ] (10 <sup>13</sup> cm <sup>-3</sup> )	Fluence/mJ cm <sup>-2</sup>	[O](10 <sup>11</sup> cm <sup>-3</sup> )	[Reactant](10 <sup>13</sup> cm <sup>-3</sup> ) <sup>b</sup>	Yield (2σ) <sup>c</sup>	No. of Expt's <sup>d</sup>
N <sub>2</sub>	198	0.17	24	6	9.12–45.2	0.122 ± 0.012	7
N <sub>2</sub>	221	0.17	24	6	13.3–53.7	0.124 ± 0.002	7
N <sub>2</sub>	251	0.18	24	6	16.5–66.4	0.120 ± 0.010	7
N <sub>2</sub>	294	0.21	24	7	8.81–73.6	0.131 ± 0.008	9
N <sub>2</sub>	294	0.16	32	7	12.5–50.4	0.126 ± 0.020	7
N <sub>2</sub>	295	0.14	24	5	12.5–48.6	0.131 ± 0.008	7
N <sub>2</sub>	295	0.28	38	15	19.2–73.7	0.122 ± 0.022	5
N <sub>2</sub>	299	0.10	32	4	11.0–70.4	0.117 ± 0.004	7
N <sub>2</sub>	362	0.18	24	6	9.13–31.8	0.123 ± 0.008	6
N <sub>2</sub>	391	0.22	24	7	9.54–62.8	0.123 ± 0.006	7
N <sub>2</sub>	427	0.22	24	7	7.94–59.1	0.122 ± 0.014	7
O <sub>2</sub>	197	0.063	36	3	4.27–27.8	0.122 ± 0.022	8
O <sub>2</sub>	237	0.065	36	3	7.75–31.4	0.118 ± 0.018	7
O <sub>2</sub>	294	0.11	32	5	7.28–49.6	0.107 ± 0.018	9
O <sub>2</sub>	295	0.059	36	3	10.1–42.8	0.118 ± 0.008	6
O <sub>2</sub>	295	0.14	24	5	5.63–38.9	0.122 ± 0.038	6
O <sub>2</sub>	366	0.078	20	2	8.72–40.4	0.095 ± 0.024	7
O <sub>2</sub>	424	0.079	38	4	8.11–43.6	0.117 ± 0.014	8
Zero air	196	0.079	24	3	4.61–41.4	0.112 ± 0.010	8
Zero air	236	0.10	24	3	10.0–42.3	0.110 ± 0.020	7
Zero air	295	0.12	24	4	7.60–41.0	0.127 ± 0.006	8
Zero air	295	0.11	28	4	7.36–27.7	0.121 ± 0.008	6
Zero air	422	0.10	28	4	5.85–43.5	0.119 ± 0.014	9

<sup>a</sup> All experiments were carried out at 20 Torr total pressure (He bath gas) with a linear rate flow through the reaction cell of 25 ± 3 cm s<sup>-1</sup> and a laser repetition rate of 10 Hz. <sup>b</sup> In addition to the concentration ranges specified, one or two experiments were always carried out with [reactant] = zero. <sup>c</sup> Precision only. <sup>d</sup> Expt. ≡ measurement and analysis of a single O(<sup>3</sup>P) temporal profile.

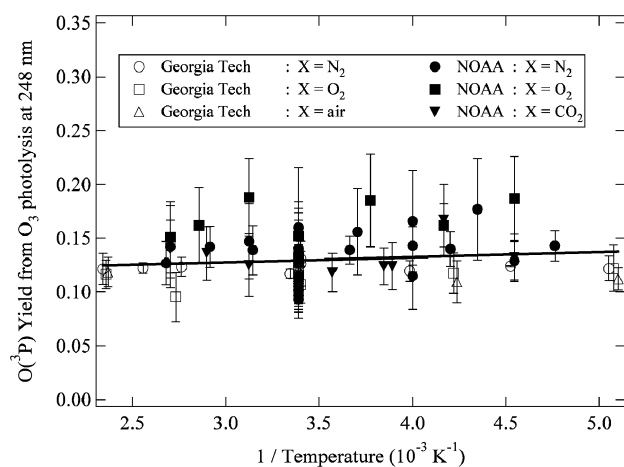
with decreasing temperature is predicted with ~75% confidence.

Lastly, we turn to the yield of O(<sup>3</sup>P) in the reaction of O(<sup>1</sup>D) with O<sub>3</sub>, O<sub>2</sub>, and its possible temperature dependence. The determination of the yield of O(<sup>3</sup>P) from the photolysis of O<sub>3</sub>, Φ<sub>O<sub>3</sub>P</sub>, involves the assumption of a unity yield of O(<sup>3</sup>P) from the reactions that convert O(<sup>1</sup>D) to O(<sup>3</sup>P). For the determinations of Φ<sub>O<sub>3</sub>P</sub> from O(<sup>1</sup>D) + O<sub>3</sub> experiments, it is assumed that O<sub>2</sub> is unity, while for determinations of Φ<sub>O<sub>3</sub>P</sub> from O(<sup>1</sup>D) + N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> or air experiments, it is assumed that O<sub>3</sub> is unity. As discussed above, O<sub>3</sub> can be assumed to be equal to 1.00 independent of temperature, whereas O<sub>2</sub> is thought to be close to unity at room temperature, but, to our knowledge, has only been measured indirectly as a function of temperature once previously.<sup>24</sup> To examine the temperature dependence of O<sub>2</sub>,

we plot the ratio of the apparent yield of O(<sup>3</sup>P) from our O<sub>3</sub> experiments, Φ<sub>O<sub>3</sub>P</sub>(O<sub>3</sub>), divided by the average yield of O(<sup>3</sup>P) from all the quencher experiments, Φ<sub>O<sub>3</sub>P</sub>(X), as a function of temperature (see Table 3 and Fig. 4). At the higher temperatures investigated in this study the ratio is close to unity, but it becomes significantly lower than unity at the lower temperatures investigated. The data are well-described by the following relationship:

$$\frac{\Phi_{O_3P}(O_3)}{\Phi_{O_3P}(X)} = (1.34 \pm 0.40) \times \exp\left(\frac{(-110 \pm 60)}{T}\right) \quad (X)$$

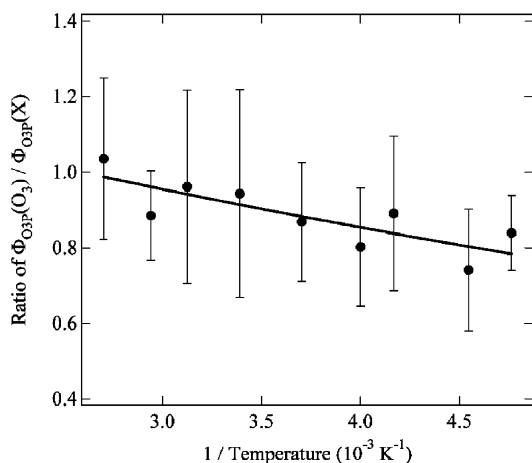
The ratio of Φ<sub>O<sub>3</sub>P</sub>(O<sub>3</sub>)/Φ<sub>O<sub>3</sub>P</sub>(X) is not a direct measurement of the ratio of O<sub>2</sub>/O<sub>3</sub>, but its temperature dependence shows that reaction (2) produces more than 1 O(<sup>3</sup>P) atom per O(<sup>1</sup>D) atom at temperatures below room temperature. At T ~ 220 K, our data suggest that the O(<sup>3</sup>P) yield from O(<sup>1</sup>D) + O<sub>3</sub> (O<sub>2</sub>) is 1.35 ± 0.29. We note that there is no reason as to why O<sub>2</sub> has to be unity even though earlier work suggests that it is close to unity at room temperature. This result agrees with the previous study of Talukdar *et al.*<sup>24</sup> within the combined uncertainties, where they found no temperature dependence for Φ<sub>O<sub>3</sub>P</sub> as measured in their O(<sup>1</sup>D) + O<sub>3</sub> experiments, *i.e.*, Φ<sub>O<sub>3</sub>P</sub>(O<sub>3</sub>),



**Fig. 3** The calculated O(<sup>3</sup>P) quantum yield from 248 nm O<sub>3</sub> photolysis plotted versus the inverse of the temperature for O(<sup>1</sup>D) + X experiments, where X = N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> or air, *i.e.*, a quencher of O(<sup>1</sup>D). The agreement between the NOAA and Georgia Tech sets of measurements is excellent and our combined results are fit to the exponential expression (2σ uncertainties): Φ<sub>O<sub>3</sub>P</sub> = (0.115 ± 0.030) × exp{(35 ± 60)/T} (solid line).

**Table 3** Averaged quantum yields for O(<sup>3</sup>P) from O<sub>3</sub> photolysis from the experiments involving O(<sup>1</sup>D) + O<sub>3</sub> and O(<sup>1</sup>D) + X (X = N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and air) as a function of temperature

Temp./K	Φ <sub>O<sub>3</sub>P</sub> (O <sub>3</sub> )	Φ <sub>O<sub>3</sub>P</sub> (X)	Φ <sub>O<sub>3</sub>P</sub> (O <sub>3</sub> )/Φ <sub>O<sub>3</sub>P</sub> (X)
210	0.120 ± 0.008	0.143 ± 0.014	0.839 ± 0.099
220	0.106 ± 0.006	0.143 ± 0.030	0.741 ± 0.161
240	0.124 ± 0.017	0.139 ± 0.026	0.891 ± 0.205
250	0.109 ± 0.010	0.136 ± 0.024	0.802 ± 0.157
270	0.139 ± 0.015	0.160 ± 0.023	0.869 ± 0.157
295	0.115 ± 0.030	0.122 ± 0.016	0.943 ± 0.275
320	0.144 ± 0.028	0.150 ± 0.027	0.962 ± 0.255
340	0.123 ± 0.016	0.139 ± 0.004	0.885 ± 0.118
370	0.145 ± 0.028	0.140 ± 0.010	1.036 ± 0.213



**Fig. 4** Ratio of the apparent yield of  $O(^3P)$  from the photolysis of  $O_3$  at 248 nm determined in the  $O(^1D) + O_3$  experiments to that in the  $O(^1D) + X$  experiments plotted as a function of temperature. The data are fit to an exponential equation ( $2\sigma$  uncertainties):  $\Phi_{O_3P}(O_3)/\Phi_{O_3P}(X) = (1.34 \pm 0.40) \times \exp\{(-110 \pm 60)/T\}$  (solid line).

and thus concluded no temperature dependence for  $\Theta_2$  as well. We believe our results here supersede those of Talukdar *et al.*<sup>24</sup>, because we incorporate a larger number of experiments involving more reactants as well as a larger number of temperatures. Once  $\Theta_2$  and its temperature dependence measured here is confirmed, the data on  $O(^1D)$  quantum yields in the photolysis of ozone from studies, such as those from Talukdar *et al.*<sup>24</sup>, can be re-evaluated. Such a re-evaluation will make small, but possibly significant, changes to the reported quantum yields in  $O_3$  photolysis at 298 K as well as a function of temperature.

In conclusion, the quantum yield for  $O(^3P)$  production from the photolysis of  $O_3$  at 248 nm has been evaluated from  $O(^3P)$  temporal profiles recorded during  $O(^1D)$  rate coefficient measurements over the temperature range (196–427) K that were conducted independently in two separate laboratories. The results agree well with each other and with previous measurements at room temperature, and they show a statistically insignificant temperature dependence for the yield of  $O(^3P)$  from  $O_3$  photolysis at 248 nm. The experiments performed here covered a wider temperature range and employed a larger number of non-reactive collision partners than the previous temperature dependent study,<sup>24</sup> reducing potential systematic errors in reported values for  $\Phi_{O_3P}(T)$  and  $\Phi_{O^1D}(T)$ , and allowing for a measurement of the temperature dependence for the yield of  $O(^3P)$  from the reaction of  $O(^1D) + O_3$ . We believe this constitutes the first measurement of this temperature dependence of  $\Theta_2$ .

## Acknowledgements

Research at Georgia Tech was supported by grants NAG5-8931 and NAG5-12987 from the NASA Upper Atmosphere Research Program. Research at NOAA was funded in part by NASA's Upper Atmosphere Research Project and NASA's Earth System Science Doctoral Fellowship to E. J. D.

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