

## THE PHOTOLYSIS OF OZONE

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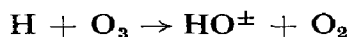
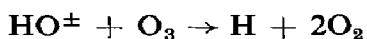
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### SUMMARY

Ozone was photolyzed at 25° C with steady illumination at several wavelengths from 2288 to 2850 Å, at O<sub>3</sub> pressures from 0.1 to 2.7 Torr, and at absorbed intensities, I<sub>a</sub>, from 0.15 to 65 mTorr/min. Experiments were done in pure dry O<sub>3</sub>, and in the presence of He, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, N<sub>2</sub>O, He-CO<sub>2</sub>, He-H<sub>2</sub>O, CO<sub>2</sub>-H<sub>2</sub>O, O<sub>2</sub>-N<sub>2</sub>O, CO<sub>2</sub>-O<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>-O<sub>2</sub>-CO<sub>2</sub> mixtures.

The results show that in the absence of added gases or in the presence of He, the quantum yield of O<sub>3</sub> consumption,  $-\Phi\{O_3\}$ , is 5.5 independent of conditions, except at pressures below 0.4 Torr, where the yield drops towards 5.0 because of wall deactivation. In the presence of CO<sub>2</sub> or N<sub>2</sub>,  $-\Phi\{O_3\}$  falls towards 4.0. The complete mechanism is outlined and it does not involve regeneration of O(<sup>1</sup>D) in the chain step. The primary photolytic act produces O(<sup>1</sup>D) and singlet O<sub>2</sub>, presumably O<sub>2</sub>(<sup>1</sup>Δ), at all wavelengths below 3000 Å.

With H<sub>2</sub>O present  $-\Phi\{O_3\}$  increases in a chain reaction whose importance is proportional to [O<sub>3</sub>] at constant [O<sub>3</sub>]/[H<sub>2</sub>O] ratios, varies inversely as I<sub>a</sub><sup>1/2</sup>, and increases with [H<sub>2</sub>O]<sup>1/2</sup> at low H<sub>2</sub>O vapor pressures, but becomes invariant or falls slightly with further increases in H<sub>2</sub>O vapor pressure. The water chain is carried by the reactions:



with HO<sup>±</sup> being vibrationally excited HO with  $\nu \geq 2$ . The chain is terminated by radical-radical processes at low H<sub>2</sub>O vapor pressures, but deactivation of HO<sup>±</sup> by H<sub>2</sub>O vapor can play a role at high H<sub>2</sub>O vapor pressures. Some wall deactivation may also occur, but it is minor in our experiments.

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In the presence of  $\text{N}_2\text{O}$ ,  $-\Phi\{\text{O}_3\}$  falls towards 4.0 at low conversions but reaches 2.8 at extended conversions. This decrease is not due to  $\text{O}_2$  accumulation but to  $\text{N}_2\text{O}_5$  accumulation which removes either  $\text{O}(^3\text{P})$  or  $\text{O}_2(^1\Delta)$ .

Relative quenching constants for  $\text{O}(^1\text{D})$  removal by various gases were measured at 2288, 2537, and 2800 Å. In some cases the results are badly scattered, but they can be summarized as follows: for  $\text{O}_3$ ,  $\text{CO}_2$ , and  $\text{N}_2$ , the relative rates are 1.0/0.4–0.5/0.08–0.11 at all wavelengths. For  $\text{H}_2\text{O}$  the constant at 2537 Å is 1.5 relative to that for  $\text{O}_3$ . With  $\text{N}_2\text{O}$ , a noticeable wavelength effect is observed and the relative rate constants are 1.5, 2–3, and 4.0 for  $\text{O}_3$  compared to  $\text{N}_2\text{O}$  at 2800, 2537, and 2288 Å, respectively. This variation must be due to the excess translational energy, which changes with wavelength, in the  $\text{O}(^1\text{D})$  atom and agrees with previous results from our laboratory.

## INTRODUCTION

The photolysis of  $\text{O}_3$  is the most important photochemical process in the upper atmosphere below about 70 km. Not only is the primary photodecomposition efficiency equal to one, but both the  $\text{O}_2$  and  $\text{O}$  fragments are electronically excited. Therefore it is important to understand the primary process in detail.

### *Dry ozone*

The photolysis of  $\text{O}_3$  has been studied for a long time. The results to 1930 were summarized by Schumacher<sup>1</sup>. In the 1930's the problem was again examined by Heidt and Forbes<sup>2–4</sup>. In dry  $\text{O}_3$ , the photolysis was studied at 2080, 2540, and 2800 Å in the presence of  $\text{O}_2$  at total pressures of 230–620 Torr and partial pressures of 35–430 Torr and 15–585 Torr for  $\text{O}_3$  and  $\text{O}_2$ , respectively<sup>3</sup>. In some cases the quantum yield for  $\text{O}_3$  disappearance was as high as 6.7, indicating that an energy chain must be present.

This problem then lay dormant for over two decades, until McGrath and Norrish<sup>5,6</sup> examined the flash photolysis. In their first paper<sup>5</sup> they used kinetic spectroscopy and observed large amounts of vibrationally excited  $\text{O}_2$  in its ground electronic state,  $^3\Sigma_g^-$ , with  $\nu \leq 17$ . In their second paper<sup>6</sup>, they added  $\text{H}_2\text{O}$  vapor and found that the vibrationally excited  $\text{O}_2$  could be completely suppressed and replaced by HO radicals. Combining their observations with those of Heidt and Forbes they proposed the now well-known mechanism for  $\text{O}_3$  photodecomposition.



The efficiency of reaction (1a) was not known, and possibly  $O_2(^3\Sigma_g^-)$ ,  $O_2(^1\Sigma_g^+)$ , and  $O(^3P)$  were also produced in that reaction. They believed that  $O_2^*$  formed in reaction (3a) was the vibrationally excited  $O_2$  which they had observed, and that it carried the energy chain *via*:



It is not clear that their experiments prove that the chain carrier  $O_2^*$  formed in reaction (3a) is vibrationally excited  $O_2$  since their experiments were performed in a large excess of  $N_2$  which has since been shown to be an efficient deactivator for  $O(^1D)$ , converting it to  $O(^3P)^{7-12}$ . The vibrationally excited  $O_2$  may come from reaction (4), which is known from the visible photolysis of  $O_3$  not to propagate chains<sup>13,14</sup>.

Conclusive evidence that  $O(^1D)$  was produced came from the observation of HO radicals in the experiments in the presence of  $H_2O$  vapor, since  $O(^3P)$  does not have sufficient energy to react with  $H_2O$  to produce HO. Because the vibrationally excited  $O_2$  could be eliminated completely in the presence of  $H_2O$ , it can be inferred that  $H_2O$  efficiently deactivates vibrationally excited  $O_2$ . The work of DeMore and Raper<sup>7,15</sup> showed that the efficiency of  $O(^1D)$  production in reaction (1) was 1.0 for photolysis at wavelengths  $< 3000 \text{ \AA}$ .

In 1965, Norrish and Wayne<sup>16</sup> published their studies on the continuous low-intensity photolysis at  $2537 \text{ \AA}$  of dry  $O_3$  at 2–50 Torr. They found that at high pressures the quantum yield of  $O_3$  decomposition,  $-\Phi\{O_3\}$ , rose to as high as 16.7 (at 50 Torr  $O_3$ ). There was no effect of absorbed intensity, but different results were obtained in two different cells which suggested the presence of wall reactions. In both cells the low-pressure extrapolated value of  $-\Phi\{O_3\}$  was near 4.0. Thus they concluded that with the addition of a wall-terminating step for  $O_2^*$ :



their results were consistent with the McGrath and Norrish mechanism. In the presence of  $N_2$  or  $CO_2$ , the limiting quantum yield for  $O_3$  disappearance at high pressures of added gas,  $-\Phi_\infty\{O_3\}$ , approached two, which would be expected if the added gas quenched both  $O(^1D)$  and  $O_2(^1\Delta)$ . With added  $O_2$ ,  $-\Phi_\infty\{O_3\}$  approached zero which was expected since  $O_2$  can quench  $O(^1D)$  and react with  $O(^3P)$ :



At this point the problem appeared solved except for the details. It was still necessary to determine the efficiency of  $O_2(^1\Delta)$  production, or if  $O_2(^1\Sigma_g^+)$  was produced in reaction (1). Also the nature of  $O_2^*$  and the efficiency of its production were still unknown.

Soon, however, discrepancies appeared. The first anomaly concerned the fate of  $O_2(^1\Delta)$ . That it can react with  $O_3$  *via* reaction (2) had been established and the

rate constant had been determined<sup>17</sup>. Subsequent investigations<sup>18–21</sup> have confirmed the reaction. Though the rate constant is not large, it is still large enough to completely consume all the  $O_2(^1\Delta)$ . The reactivity of  $O_2(^1\Delta)$  with  $N_2$  or  $CO_2$  is negligible<sup>22,23</sup>, and these molecules could not possibly quench the reaction and drop  $-\Phi\{O_3\}$  to 2.0.

Possibly the discrepancy could be explained by the formation of  $O_2(^1\Sigma_g^+)$  rather than  $O_2(^1\Delta)$  in reaction (1). Evidence for this possibility was put forth by Izod and Wayne<sup>24</sup>. Though they detected the emission from  $O_2(^1\Delta)$  at  $1.27\ \mu\text{m}$  in the photolysis of  $O_3$ , they argued that it arose from the secondary reaction of  $O(^1D)$  with  $O_2$ , since they could only see the signal in the presence of  $O_2$ . No  $O_2(^1\Delta)$  was detected when  $N_2$  or Ar replaced  $O_2$ . That  $O_2(^1\Sigma_g^+)$  reacts readily with  $O_3$  had been established<sup>18</sup>, and subsequently confirmed<sup>25</sup>. However, again the reactivity of  $O_2(^1\Sigma_g^+)$  with  $N_2$  or  $CO_2$  is much too slow to have permitted quenching by these gases<sup>11,26</sup>. Furthermore, Gauthier and Snelling<sup>27</sup>, as well as Gilpin *et al.*<sup>28</sup>, have shown that at  $2537\ \text{\AA}$  (Gilpin *et al.* used radiation between  $2375$  and  $2625\ \text{\AA}$ ) only  $O_2(^1\Delta)$  is produced in reaction (1) ( $<5\%$   $^1\Sigma_g^+$ ) and that the  $O_2(^1\Sigma_g^+)$ , but little or none of the  $O_2(^1\Delta)$ , comes from the interaction of  $O(^1D)$  with  $O_2$  in conformance with Noxon's findings<sup>29</sup>:



Wayne has also come to this conclusion in more recent work<sup>30</sup>.

Further experiments were done by Wayne and White<sup>31</sup>, who studied the photolysis in a flow system at  $O_3$  pressures less than 1 Torr. They only obtained relative quantum yields, but they found that these dropped by a factor of 5 as the  $O_3$  pressure was reduced from 0.67 to 0.10 Torr. Wayne has privately informed us that these observations were incorrect.

Jones *et al.*<sup>32</sup> returned to the flow system and photolyzed dry  $O_3$  at  $2537\ \text{\AA}$  in the presence of 10–90%  $O_2$  at total pressures of 0.1–2 Torr. The  $O_3$  pressures were between 0.05 and 2 Torr, and in these experiments  $-\Phi\{O_3\}$  was close to 4 independent of either the  $O_3$  or  $O_2$  pressure. (Actually  $-\Phi\{O_3\}$  was 4.5 with 10%  $O_2$  and this dropped to 3.5 with 90%  $O_2$ .) Presumably under these conditions, reaction (5a) is unimportant compared to reaction (6) and the results conform to those in a static system at low pressure.

Jones and Wayne<sup>33</sup> rechecked the results of Norrish and Wayne at  $2537\ \text{\AA}$  and corroborated the earlier findings. Jones and Wayne also examined the photolysis at  $3130$  and  $3340\ \text{\AA}$ , where there is insufficient energy to produce both  $O(^1D)$  and  $O_2(^1\Delta)$ . Since  $-\Phi\{O_3\}$  was still about 4.0, the products of reaction (1) could not have been  $O(^1D)$  and singlet  $O_2$ . (At  $3130\ \text{\AA}$ , there is sufficient thermal energy to product  $O(^1D)$  and  $O_2(^1\Delta)$  about 10% of the time, and  $-\Phi\{O_3\}$  can be slightly greater than 4.0.) At about the same time, more extensive studies of Castellano and Schumacher<sup>34</sup> indicated that  $-\Phi\{O_3\} = 6.0$  at  $3130\ \text{\AA}$  for short irradiation times.

Finally Jones and Wayne<sup>35</sup> extended the measurements to six wavelengths

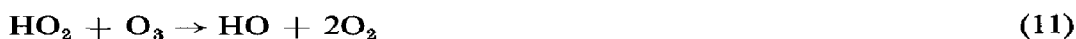
between 2480 and 3340 Å. The quantum yield of O<sub>3</sub> consumption increased with the O<sub>3</sub> pressure as at 2537 Å. A long extrapolation of rather scattered data indicated a low-pressure intercept of 4.0 in each case. At 3340 Å, some experiments were done with H<sub>2</sub> added to test for the presence of O(<sup>1</sup>D), since O(<sup>1</sup>D) reacts with H<sub>2</sub> to give a long chain decomposition of O<sub>3</sub>. The experiments confirmed that only O(<sup>3</sup>P) was produced at this wavelength.

At about the time that our experiments were initiated, a paper appeared by Webster and Bair<sup>36</sup> which cast doubt on some aspects of the McGrath–Norrish mechanism. Webster and Bair photolyzed 0.2 Torr of O<sub>3</sub> in a static system with steady illumination at 2537 Å. They worked at very low decomposition (0.5–1%), and only measured relative quantum yields. They found that the addition of N<sub>2</sub> reduced  $-\Phi\{O_3\}$ , as had Norrish and Wayne<sup>16</sup>. However, realizing that N<sub>2</sub> could not quench O<sub>2</sub>(<sup>1</sup>Δ), they assumed that  $-\Phi_\infty\{O_3\} = 4.0$ , rather than 2.0 found by Norrish and Wayne. In the absence of N<sub>2</sub>,  $-\Phi\{O_3\}$  would then be ~5.0. The addition of He, which does not quench O(<sup>1</sup>D)<sup>37–39</sup>, raised the yield slightly to about 50% greater than that in excess N<sub>2</sub>. From these results Webster and Bair concluded that O<sub>2</sub>\* did not undergo reaction (5a) but rather that O<sub>2</sub>\* was really two O(<sup>3</sup>P) atoms. The enhancement effect of He was then to minimize loss of O(<sup>3</sup>P) on the wall. Because of the long lifetime needed for O<sub>2</sub>\* (τ > 10<sup>-3</sup> sec), the <sup>3</sup>Σ<sub>u</sub><sup>-</sup> and <sup>3</sup>Σ<sub>u</sub><sup>+</sup> states of O<sub>2</sub> were excluded as possibilities.

#### *Wet ozone*

It was Warburg<sup>40</sup> who first found that the photodecomposition of O<sub>3</sub> was enhanced in the presence of water. Forbes and Heidt<sup>2</sup> made a quantitative study with radiation at 2800, 2540, and 2100 Å and O<sub>3</sub> pressures between 10 and 760 Torr. They found that  $-\Phi\{O_3\}$  could rise to as high as 130, and that it was proportional to [H<sub>2</sub>O] and dropped as the absorbed intensity, *I<sub>a</sub>*, was raised. The intensity effect suggests a radical–radical termination step, but Norrish and Wayne<sup>41</sup> found little change in  $-\Phi\{O_3\}$  with intensity and concluded that radical–radical termination was unimportant.

McGrath and Norrish<sup>6,42</sup> demonstrated the presence of HO radicals in the flash photolysis and proposed the following steps to propagate the chain:



In further experiments Basco and Norrish<sup>43</sup> demonstrated that up to 2 quanta of vibrational energy could be present in the HO radical.

It was DeMore<sup>44</sup> who pointed out, from a comparison with Kaufman's results<sup>45</sup>, that reactions (10) and (11) were unsatisfactory. DeMore proposed that the chain steps were:



where  $\text{HO}^\pm$  is vibrationally excited HO. Support for this hypothesis was soon given<sup>46</sup> in the liquid phase photolysis of  $\text{O}_3$  at  $-186^\circ\text{C}$ . The addition of  $\text{O}_2$  suppressed the chain indicating that  $\text{O}_2$  scavenged the H atoms and that  $\text{HO}_2$  did not react with  $\text{O}_3$ , at least at low temperatures in the liquid phase. Confirmation that  $\text{HO}^\pm$  ( $\nu = 9$ ) formed in reaction (13) reacted rapidly with  $\text{O}_3$  was given by Potter *et al.*<sup>47</sup>.

Recent flash photolysis studies<sup>48, 49</sup> have shown that  $-\Phi\{\text{O}_3\}$  is not increased in the presence of water vapor and that HO ( $\nu = 0,1$ ) is essentially unreactive to  $\text{O}_3$ . Thus it is not clear how the chains are initiated in the steady illumination experiments. Langley and McGrath<sup>49</sup> have suggested that some  $\text{H}_2\text{O}_2$  might be produced *via*:



and that the reaction of  $\text{O}(^1\text{D})$  with  $\text{H}_2\text{O}_2$  would produce  $\text{HO}(\nu = 3)$  to start the chain. Another possible route to  $\text{H}_2\text{O}_2$  production is direct insertion:



### *Present status*

At present the  $\text{O}_3$  photolysis can be summarized as follows. The initial photodecomposition proceeds with unit efficiency. For wavelengths below 3000 Å,  $\text{O}(^1\text{D})$  is the exclusive O-atom product; at 3340 Å,  $\text{O}(^3\text{P})$  is the exclusive O-atom product; and at 3130 Å,  $\text{O}(^3\text{P})$  is the main O-atom product ( $\geq 90\%$ ). At 3130 and 3340 Å, singlet  $\text{O}_2$  is produced, but it may be either  $\text{O}_2(^1\Delta)$  or  $\text{O}_2(^1\Sigma_g^+)$ . At lower wavelengths, only  $\text{O}_2(^3\Sigma_g^-)$  or  $\text{O}_2(^1\Delta)$  is energetically possible until wavelengths  $< 2660$  Å are reached; then  $\text{O}_2(^1\Sigma_g^+)$  could also be produced, though it apparently is not at 2537 Å. Recent absolute measurements for  $-\Phi\{\text{O}_3\}$  below 3100 Å are those of Wayne and his coworkers, who found  $-\Phi\{\text{O}_3\} = 2.0$  in the presence of a large excess of  $\text{CO}_2$  or  $\text{N}_2$ . However, this value was obtained for extended conversions so that reaction (7) may be playing a role. In a paper that came to our attention after our manuscript was prepared, von Ellenrieder *et al.*<sup>49a</sup> reported that, with 2537 Å radiation,  $-\Phi\{\text{O}_3\} = 6.0$  in the absence of added gases, but this value drops to 4.0 in the presence of a large excess of  $\text{N}_2$ .

Singlet  $\text{O}_2$  (either  $^1\Delta$  or  $^1\Sigma_g^+$ ) is removed exclusively by reaction with  $\text{O}_3$ , and  $\text{O}(^3\text{P})$  can be removed either by reaction (4) or (7). The nature of  $\text{O}_2^*$  formed in reaction (3a), the efficiency of its formation, and its fate are not established.

In the presence of  $\text{H}_2\text{O}$  the photodecomposition is enhanced and proceeds by a long chain process, presumably involving reactions (12) and (13). However, the chain initiating and terminating steps have not yet been found to be satisfactory in explaining all the data.

We have undertaken a re-examination of the steady-state photolysis of  $O_3$  in order to:

- (1) determine the efficiency of singlet  $O_2$  production in reaction (1) as a function of exciting wavelength;
- (2) determine the efficiency of  $O_2^*$  production in reaction (3a) and the fate of  $O_2^*$ ;
- (3) study some quenching reactions of  $O(^1D)$  with various gases as a function of exciting wavelength;
- (4) help elucidate the chain mechanism in the presence of  $H_2O$  vapor; and
- (5) study the photolysis in the presence of  $N_2O$ .

#### EXPERIMENTAL

A conventional high-vacuum line utilizing Teflon stopcocks with Viton 'O' rings was used. Both mercury and stopcock grease were rigorously excluded. Pressures were measured with a sulfuric acid manometer, a NRC alphanatron gauge or a Veeco thermocouple gauge. Pressures of  $O_3$  lower than 100 mTorr were measured by expanding a higher pressure into a calibrated volume. Ozone was always measured with the sulfuric acid manometer and was never introduced into either the alphanatron or the thermocouple gauge. When ozone was added as a second gas into the reaction cell, its concentration was determined from its optical absorption. Calibration curves of light absorption vs. ozone pressure were made at all wavelengths. At 2537 Å, Beer's law was obeyed and the extinction coefficient agreed with that in the literature<sup>50</sup>. At 2288 and 2800 Å, the irradiation was not monochromatic and the Beer's law plots were curved. Concentrations were determined from these plots directly.

The reaction cell was a cylindrical quartz cell 10 cm long and 5 cm in diameter. During a run the ozone concentration was monitored continuously from its light absorption. To obtain the rate of photodecomposition for low conversions, a method utilizing the simultaneously measured difference between the incident and transmitted radiation was employed. It permitted determination of decomposition rates at conversions of <1%. Dark decomposition of the ozone, as well as changes of concentration due to mixing, were negligible under all the conditions employed.

The wavelengths of the irradiation were obtained by use of:

2288 Å—a Phillips Cd resonance lamp Typ. 93107E plus a chlorine gas filter (300 Torr and 5 cm in length) to remove radiation >3000 Å and a Corning 9-30 filter to remove radiation below 2200 Å. In addition to the 2288 Å line, the weaker 2265 Å line was also passed;

2537 Å—a Hanovia flat-spiral low-pressure Hg resonance lamp Model No. Z1400-013 plus the chlorine and Corning 9-30 filters, as well as a Corning 7-54 filter which only passes radiation between 2300 and 4200 Å;

2800 Å—a high pressure 150 W Osram xenon arc lamp with a Jarrell-Ash

1/4 m Ebert monochromator, Model 82-410 with 2 mm slit widths. The band pass at 1/2 height was about 100 Å.

Actinometry was done at each wavelength by measuring the amount of products obtained when substances of known behavior were photolyzed under similar conditions. In all cases the light absorption was matched to that in the corresponding O<sub>3</sub> photolysis. At 2288 and 2537 Å, HBr was used. Its photolysis gives H<sub>2</sub> with a quantum yield of one<sup>51</sup>. At 2800 Å, HI was used. It was assumed that  $-\Phi\{\text{H}_2\}$  was unity as it is at lower wavelengths<sup>52</sup>.  $I_a$  is reported in units of mTorr/min of H<sub>2</sub> produced, and can be converted to Einstein/liter-min by dividing by  $1.86 \times 10^7$ .

Ozone was prepared by passing an electric discharge through Air Products Research Grade O<sub>2</sub>. The O<sub>3</sub> produced was collected at  $-196^\circ\text{C}$ , and the excess O<sub>2</sub> was pumped away. The O<sub>3</sub> was then distilled at  $-186^\circ\text{C}$ , stored at  $-196^\circ\text{C}$ , and degassed at this temperature before each run. Matheson N<sub>2</sub>O and Bone Dry CO<sub>2</sub> were distilled trap to trap, the medium fractions being retained. Air Products Research Grade N<sub>2</sub> and Matheson He were used without purification. Both distilled H<sub>2</sub>O and tap water were used after degassing at  $-50^\circ\text{C}$ . The results were similar with either source of H<sub>2</sub>O. The actinometer gases were Matheson HBr and HI which were distilled at  $-100^\circ\text{C}$  to remove the corresponding halogen and degassed at  $-196^\circ\text{C}$  before use.

#### PHOTOLYSIS OF DRY OZONE

##### *Results*

Pure dry O<sub>3</sub> was photolyzed at 2800, 2537, and 2288 Å. At each wavelength, the pressure of O<sub>3</sub> was used which gave the maximum percentage change in transmission of the radiation for a given percentage decomposition. Initially the quantum yields of O<sub>3</sub> removal were irreproducible. Only after conditioning the reaction vessel by several photolyses of pure dry O<sub>3</sub> to high conversions could reproducible results be obtained. For example, after introducing HBr to the reaction cell, values of  $-\Phi\{\text{O}_3\}$  as high as 15 were obtained even after prolonged pumping of the cell to pressures below 1 mTorr. A similar effect was observed after baking the reaction cell.

For photolyses to low conversions (<3%) in the conditioned cell in the absence of any added gas the resultant quantum yields,  $-\Phi_0\{\text{O}_3\}$ , are listed in Table I. At all the wavelengths,  $-\Phi_0\{\text{O}_3\}$  is measurably greater than 4, being  $5.8 \pm 0.3$ ,  $5.0 \pm 0.3$ , and  $5.9 \pm 0.3$  for radiation at 2800, 2537, and 2288 Å, respectively. The runs at 2537 Å were with the lowest O<sub>3</sub> pressure, and some wall deactivation could have occurred, accounting for the somewhat lower value at that wavelength.

Experiments were then done with the same pressures of O<sub>3</sub>, but with either CO<sub>2</sub> or N<sub>2</sub> added. The results for low conversions at 2800, 2537, and 2288 Å, are shown in Figs. 1-4. The addition of either gas reduces  $-\Phi\{\text{O}_3\}$  to a limiting value,



TABLE I

LIMITING VALUES FOR THE OZONE PHOTODECOMPOSITION QUANTUM YIELDS

$\lambda$ (Å)	$[O_3]$ (Torr)	$I_a$ (mTorr/min)	$-\Phi_0\{O_3\}$	$-\Phi_\infty\{O_3\}$ for M =		
				CO <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O
2800	1.0	7.0	$5.8 \pm 0.3$	$4.25 \pm 0.4$	-	$4.15 \pm 0.5$
2537	0.24	3.0	$5.0 \pm 0.3$	$4.1 \pm 0.4$	$3.85 \pm 0.4$	$3.9 \pm 0.3$
2288	0.85	2.0	$5.9 \pm 0.3$	$4.4 \pm 0.4$	-	$4.4 \pm 0.5$

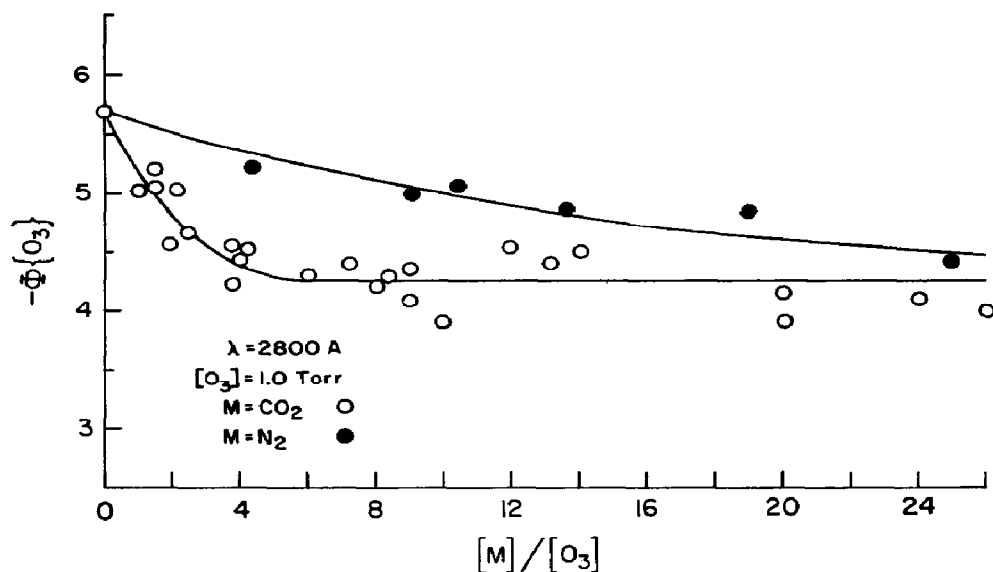


Fig. 1. Plot of the quantum yield of O<sub>3</sub> consumption vs. either [CO<sub>2</sub>]/[O<sub>3</sub>] or [N<sub>2</sub>]/[O<sub>3</sub>] in the photolysis of O<sub>3</sub>-CO<sub>2</sub> or O<sub>3</sub>-N<sub>2</sub> mixtures for short conversions at 2800 Å, 25°C [O<sub>3</sub>] ~1.0 Torr and  $I_a = 7.0$  mTorr/min.

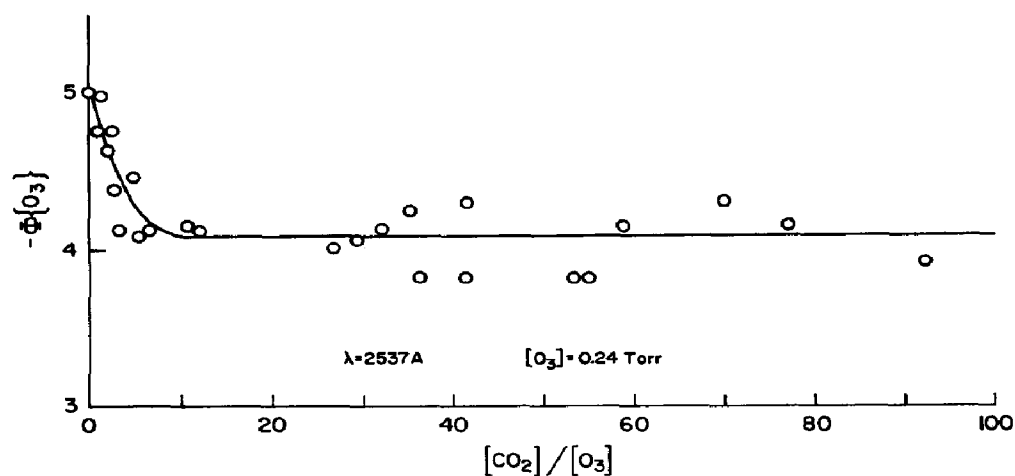


Fig. 2. Plot of the quantum yield of O<sub>3</sub> consumption vs. [CO<sub>2</sub>]/[O<sub>3</sub>] in the photolysis of O<sub>3</sub>-CO<sub>2</sub> mixtures for short conversions at 2537 Å, 25°C, [O<sub>3</sub>] = 0.24 Torr and  $I_a = 3.0$  mTorr/min.

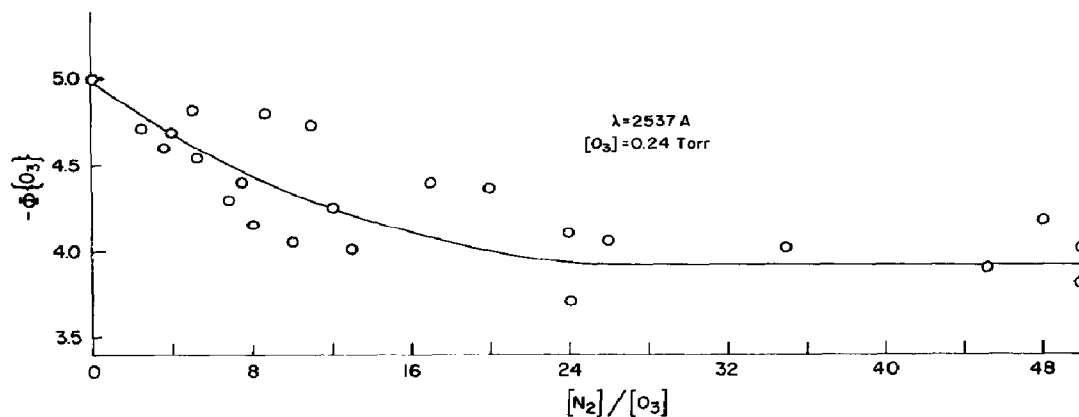


Fig. 3. Plot of the quantum yield of  $O_3$  consumption vs.  $[N_2]/[O_3]$  in the photolysis of  $O_3-N_2$  mixtures for short conversions at 2537 Å, 25°C,  $[O_3] \sim 0.24$  Torr and  $I_a = 3.0$  mTorr/min.

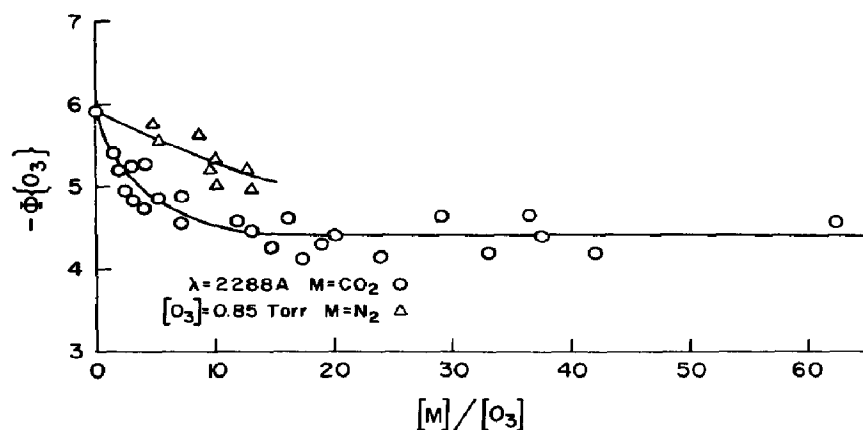


Fig. 4. Plot of the quantum yield of  $O_3$  consumption vs. either  $[CO_2]/[O_3]$  or  $[N_2]/[O_3]$  in the photolysis of  $O_3-CO_2$  or  $O_3-N_2$  mixtures for short conversions at 2288 Å, 25°C,  $[O_3] \sim 0.85$  Torr and  $I_a = 2.0$  mTorr/min.

$-\Phi_{\infty}\{O_3\}$ , of about 4.0 in agreement with that of Ellenrieder *et al.*<sup>49a</sup>; the exact values found by us are listed in Table I. The addition of 13 Torr of He in the  $CO_2$  experiments at 2537 Å had no noticeable effect. The only other absolute measurement of these values was made by Norrish and Wayne<sup>16</sup>, who found values of about 2.0. At that time they explained these low values as resulting from the quenching of singlet  $O_2$  by  $CO_2$  and  $N_2$ . It is now known that this explanation cannot be correct (see Introduction), and the low value is inconsistent with any proposed mechanism for  $O_3$  photodecomposition. The reason for the low values found by Norrish and Wayne is that in their work the percentage decomposition of the  $O_3$  was considerably larger than in our work. Thus considerable  $O_2$  was present, reaction (7) was important, and  $-\Phi_{\infty}\{O_3\}$  was reduced. That their percentage decomposition was excessive can be deduced from the half-quenching pressures of  $CO_2$  and  $N_2$  required. (They do not report the percentage decomposition in their

paper, but Wayne has informed us privately that it was 10–12% for 2 Torr  $O_3$ .) Their half-quenching pressures were much too large to be consistent with the now-known values for  $O(^1D)$  deactivation (see below). To check the above argument, we performed experiments with excess  $CO_2$  for extended conversions at 2537 Å and found that  $-\Phi_{\infty}\{O_3\}$  could be considerably reduced below 4.0. It is interesting to note that for  $[O_3] = 2$  Torr, Norrish and Wayne<sup>16</sup>, found  $-\Phi\{O_3\} = 3.9$  for  $[CO_2] = 20$  Torr and  $-\Phi\{O_3\} > 4.2$  for  $[N_2]$  up to 100 Torr, in agreement with our findings.

The investigations of both Norrish and Wayne<sup>16</sup> and Webster and Bair<sup>30</sup> show that  $-\Phi_0\{O_3\}$  is greater than  $-\Phi_{\infty}\{O_3\}$ , in concordance with our findings. Webster and Bair report  $-\Phi_0\{O_3\} = 4.9$  at 2537 Å for  $[O_3] = 0.20$  Torr based on  $-\Phi_{\infty}\{O_3\} = 4.0$ . This result agrees exactly with ours. The addition of excess He [which does not quench  $O(^1D)$ ] raised the value to 6.0 in Webster and Bair's work, but the addition of 13 Torr of He only raised our value by 6%. However, the experimental uncertainties in both measurements are such that this discrepancy is not alarming. (Actually as we shall show, in excess He the value should be  $5.5 \pm 0.3$ .)

Further substantiation that  $-\Phi_0\{O_3\}$  is greater than 4.0 comes from the work of Heidt and Forbes<sup>3</sup>. Their results, which were obtained in the presence of  $O_2$ , are plotted in Fig. 5 vs. the ratio  $[O_2][M]/[O_3]$ . The abscissa is the parameter which determines the relative importance of reactions (7) and (4). At high values of the abscissa, reaction (7) is important, and  $-\Phi\{O_3\}$  is as low as 2.3. However, as reaction (7) becomes less important,  $-\Phi\{O_3\}$  rises; the value of  $-\Phi\{O_3\}$  extra-

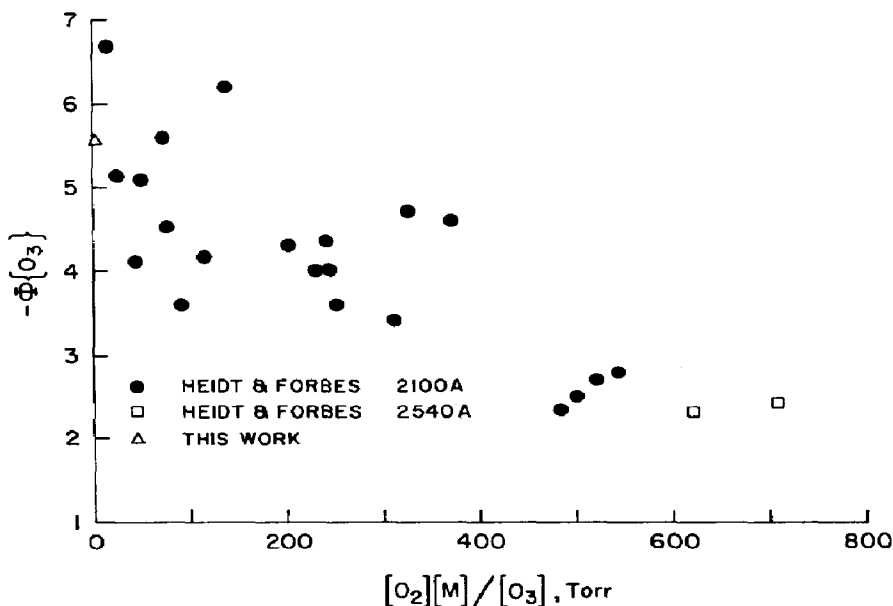


Fig. 5. Plot of the quantum yield of  $O_3$  consumption vs.  $[O_2][M]/[O_3]$  in the work of Heidt and Forbes<sup>3</sup>.

polated to  $[O_2][M]/[O_3] = 0$  is in good agreement with ours, though the Heidt and Forbes data are badly scattered.

The flow experiments of Jones *et al.*<sup>32</sup> done at 2537 Å give  $-\Phi_0\{O_3\} = 4.5 \pm 0.3$  for mixtures of 10%  $O_2$ , and lower values for mixtures with a higher percentage of  $O_2$ . In the latter case the reduced values can be accounted for by reaction (7). The value of  $4.5 \pm 0.3$ , which does not include a stated 10% uncertainty in actinometry, in the former case is not significantly below the value of  $5.0 \pm 0.3$  obtained by us.

The only studies which indicate that  $-\Phi_0\{O_3\}$  is 4.0 at low  $O_3$  pressures are those of Wayne and his coworkers<sup>16,33,35</sup> done at 2537 Å in a static system with steady illumination. However, this conclusion is based on a long extrapolation from high-pressure results carried out to larger conversions (3–7%) than used by us. Furthermore there are other problems in these studies (see below). We conclude that the conclusion that  $-\Phi_0\{O_3\}$  is 4.0 can be discounted.

The pressure dependence of  $-\Phi_0\{O_3\}$  was determined in a series of runs at several wavelengths. For these runs  $-\Phi_\infty\{O_3\}$  was assumed to be 4.0 in the presence of  $CO_2$ , and the values of  $-\Phi_0\{O_3\}$  are based on this assumption. The results are shown as a semi-log plot in Fig. 6.

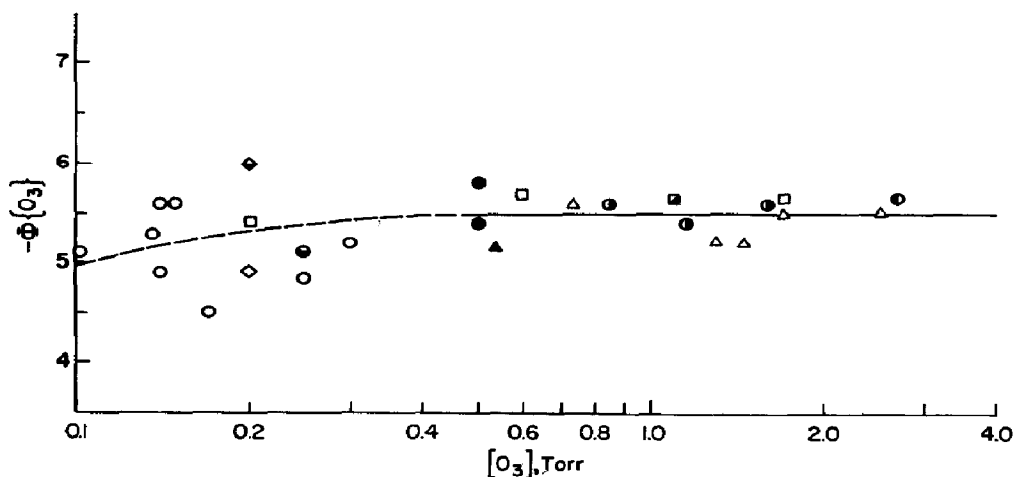


Fig. 6. Semi-log plot of the quantum yield of  $O_3$  consumption vs.  $O_3$  pressure in the photolysis of ozone at 25°C: ●, 2800 Å, after baking and conditioning cell; ○, 2537 Å; ◐, 2537 Å, 13 Torr He present; ◑, 2800 Å; ◒, 2850 Å; □, 2800 Å, traces of  $H_2O$  present; ◓, 2800 Å, 5 mTorr  $H_2O$  present; △, 2288 Å; ▲, 2400 Å; ◆, from Webster and Bair<sup>36</sup>; ◇, from Webster and Bair<sup>36</sup>, large excess of He present.

For pressures between 0.4 and 2.7 Torr,  $-\Phi_0\{O_3\}$  is invariant at  $5.5 \pm 0.3$  to pressure changes or to the wavelength of the incident radiation between 2288 and 2850 Å. Baking (followed by conditioning) the cell or adding 5 mTorr of  $H_2O$  vapor also had no effect. Experiments at pressures between 0.1 and 0.3 Torr were done at 2537 Å. The results are more scattered and  $-\Phi_0\{O_3\}$  varies from 4.5 to

TABLE II

EFFECT OF ABSORBED INTENSITY IN THE PHOTOLYSIS OF DRY O<sub>3</sub> AT 0.14 TORR AND 2537 Å

$I_a$ (mTorr/min)	$-\Phi\{O_3\}$
0.15	5.2
0.25	5.6
2.0	5.6
50	4.9
65	5.3

5.6. At these low pressures some wall deactivation, which may vary from run to run, possibly occurs, accounting for both the scatter and the fall-off in  $-\Phi_0\{O_3\}$ .

Finally the effect of absorbed intensity,  $I_a$ , was investigated and the results are in Table II. A 430-fold variation in  $I_a$  had no effect, in agreement with the findings of Norrish and Wayne<sup>16</sup>.

It is clear that  $-\Phi_0\{O_3\} = 5.5 \pm 0.3$  at low conversions for O<sub>3</sub> pressures between 0.4 and 2.7 Torr. In the absence of wall deactivation, it seems likely that this value is valid to O<sub>3</sub> pressures of 0.1 Torr or even lower. The possibility that this value is high because of the presence of H<sub>2</sub>O vapor, which greatly enhances the quantum yield, can be discounted for three reasons: (1) baking the cell (and then conditioning it by photolyzing dry O<sub>3</sub>) or adding trace amounts of H<sub>2</sub>O vapor had no effect; (2) there is no effect of O<sub>3</sub> pressure, though later we will show that in the presence of H<sub>2</sub>O, changing the O<sub>3</sub> pressure does change the results; and (3) there is no effect introduced by changing  $I_a$ , though in the presence of H<sub>2</sub>O vapor a significant change results by altering  $I_a$  (see later results).

The results of Wayne *et al.*<sup>16,33,35</sup> indicate that for O<sub>3</sub> pressures above 2 Torr,  $-\Phi_0\{O_3\}$  increases dramatically, reaching values of 16.7 at 50 Torr. Perhaps there is a dramatic shift in the O<sub>3</sub> photodecomposition mechanism at O<sub>3</sub> pressures of 2–3 Torr. This seems unlikely to us. Furthermore, Heidt and Forbes<sup>3</sup> performed experiments at O<sub>3</sub> pressures up to 428 Torr at 0°C and up to 294 Torr at room temperature, and except for two points which gave values for  $-\Phi\{O_3\} = 6.7$  and 6.3, they found that  $-\Phi\{O_3\}$  was always less than 6.0. Never did they find values even approaching those reported in the Wayne studies.

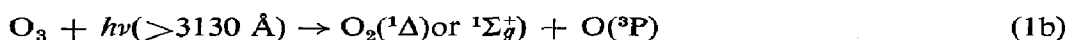
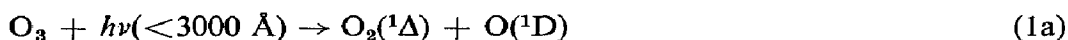
We suggest that the large values for  $-\Phi\{O_3\}$  found in the Wayne studies may be incorrect, possibly because the reaction cell was not properly conditioned. Effects similar to those observed by us after HBr had been present (*i.e.*  $-\Phi\{O_3\} \sim 15$ ) might have occurred in the Wayne studies. Excessive baking of the cell likewise produces high quantum yields. Evidence for this hypothesis comes from the work of Norrish and Wayne<sup>16</sup> in which  $-\Phi\{O_3\} < 5$  even for  $[O_3] = 17$  Torr in a 4 cm diameter cell, but  $-\Phi\{O_3\} \sim 8.0$  in a 7 cm diameter cell at the same pressure. Possibly the 7 cm diameter cell was not properly conditioned.

It should be emphasized, however, that the pressure ranges used by us and in the Wayne studies barely overlapped, and that there is no direct discrepancy in

experimental results at the pressures used in both studies. Nevertheless, von Ellenrieder *et al.*<sup>49a</sup> reported that with 2537 Å radiation  $-\Phi\{\text{O}_3\} = 6.0$  for  $\text{O}_3$  pressures between 10 and 100 Torr.

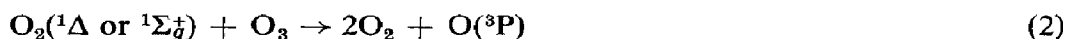
### Mechanism

The primary photochemical act is:



For radiation between about 3000 and 3130 Å, both processes (1a) and (1b) can occur, with reaction (1b) occurring about 40% of the time at about 3100 Å<sup>15</sup>. Singlet  $\text{O}_2$  is produced exclusively at all wavelengths. For process (1a), only  $\text{O}_2(^1\Delta)$  is energetically possible for radiation  $>2660 \text{ \AA}$ . With radiation at 2537 Å,  $\text{O}_2(^1\Delta)$  is certainly the dominant, if not the exclusive, state of  $\text{O}_2$ <sup>27,28</sup>. At wavelengths below 2537 Å it is not known whether some  $\text{O}_2(^1\Sigma_g^+)$  is formed. However, its presence would not affect any of the following arguments, so we will ignore this possibility.

The singlet  $\text{O}_2$  is always removed *via* reaction with  $\text{O}_3$ :



In the absence of added gases  $\text{O}(^1\text{D})$  reacts with  $\text{O}_3$ :



where  $\text{O}_2^*$  is some unspecified excited electronic state of  $\text{O}_2$  (or 2  $\text{O}(^3\text{P})$  atoms). In the absence of significant amounts of  $\text{O}_2$ , *i.e.* at low conversions, the  $\text{O}(^3\text{P})$  atom is removed in the well-known reaction:



Otherwise reaction (7) must also be involved.

Before estimating the relative importance of reactions (3a) or (3b), let us examine the fate of  $\text{O}_2^*$ . There are three possible reactions:



Reaction (5a) can be eliminated from a consideration of the results of Goldman *et al.*<sup>53</sup>. They studied the photolysis of  $\text{O}_3$  in the presence of  $\text{N}_2\text{O}$  and measured the  $\text{N}_2$  produced. Their results showed that  $\text{O}(^1\text{D})$  was not regenerated *via* reaction (5). At the time they accepted reaction (5a) and concluded that  $\text{O}_2^*$  must have been

deactivated completely by small amounts of  $N_2O$ . However, our work with  $N_2O$ , soon to be discussed, shows that in fact this is not so. Therefore, reaction (5a) is negligible. Gilpin *et al.*<sup>28</sup> have also reported that  $<10\%$  of the  $O(^1D)$  can come from chain regeneration. At very low pressures reaction (6) may play some role, but it certainly is unimportant at pressures above 0.4 Torr; reaction (5b) is the dominant fate of  $O_2^*$ .

The mechanism consisting of steps (1a), (2)–(4), and (5b) predicts that

$$-\Phi_0\{O_3\} = 4 + 2k_{3a}/k_3 \quad (I)$$

where  $k_3 = k_{3a} + k_{3b}$ . Since  $-\Phi_0\{O_3\} = 5.5 \pm 0.3$ , then  $k_{3a}/k_3 = 0.75 \pm 0.15$ .

The nature of  $O_2^*$  is of considerable interest. Webster and Bair<sup>36</sup> argued against  $O_2(^3\Sigma_u^+ \text{ or } ^3\Sigma_u^-)$ . They favored the explanation that  $O_2^*$  was in reality two  $O(^3P)$  atoms, and this possibility must be given serious consideration. As far as we know neither  $O_2(^1\Delta)$  nor  $O_2(^1\Sigma_g^+)$  is deactivated at the wall, and these possibilities for  $O_2^*$  are not likely. A more compelling (but not conclusive) argument against  $O_2(^1\Delta)$  or two  $O(^3P)$  atoms is the fact that  $-\Phi_0\{O_3\}$  does not fall below 4.0 even at 0.1 Torr pressure, as would be expected for complete removal at the wall. (In fact  $-\Phi_0\{O_3\}$  does not fall below 4.5.) Evidence against  $O_2(^1\Sigma_g^+)$  comes from the work of Gauthier and Snelling<sup>27</sup> and Gilpin *et al.*<sup>28</sup> who showed that all the  $O_2(^1\Sigma_g^+)$  could be explained by reaction (8). Consequently we feel that the most likely candidates for  $O_2^*$  are  $O_2(^1\Sigma_u^-)$  or  $O_2(^3\Delta_u)$ . The production of  $O_2(^1\Sigma_u^-)$  violates the spin conservation rules (which may or may not apply), but the production of  $O_2(^3\Delta_u)$  is spin allowed. The precise identification of  $O_2^*$  will require more work.

#### Deactivation of $O(^1D)$

In the presence of  $CO_2$  or  $N_2$ , the  $O(^1D)$  atom can be deactivated



These reactions account for the drop in  $-\Phi\{O_3\}$  with the addition of these gases for then reaction (3a) is reduced. When  $-\Phi\{O_3\} = -(\Phi_0\{O_3\} + \Phi_\infty\{O_3\})/2$ , then  $k_3[O_3] = k_{16}[CO_2]$  or  $k_{17}[N_2]$ . From the decay curves in Figs. 1–4, the values for  $k_{16}/k_3$  and  $k_{17}/k_3$  can be obtained and they are listed in Table III. The data in the figures are rather badly scattered, especially for  $N_2$  at 2537 Å, so that these determinations are not very accurate.

The only direct determination of  $k_{17}/k_3$  was made by Snelling and Bair<sup>9</sup> in the flash photolysis of  $O_3$ . They report a value of  $0.065 \pm 0.03$  in reasonable agreement with our values. The later ‘corrected’ value of  $0.50 \pm 0.25$  of Biedenkapp and Bair<sup>54</sup> is presumably incorrect, since the value they obtain for  $k_3$  is much lower than obtained by others<sup>28,53</sup>.

TABLE III  
RELATIVE QUENCHING CONSTANTS FOR O(<sup>1</sup>D)

Ratio	Irradiation wavelength (Å)		
	2288	2537	2800
$k_{16}/k_3$	$0.4 \pm 0.1$	$0.4 \pm 0.1$	$0.5 \pm 0.1$
$k_{17}/k_3$	$0.08 \pm 0.02$	$0.11 \pm 0.02$	$0.08 \pm 0.02$
$k_8/k_3$	—	—	1.5 <sup>a</sup>
$k_{21}/k_3$	0.25	~0.4	0.67

<sup>a</sup> From Fig. 7.

TABLE IV  
VALUE OF  $k_{17}/k_{16}$

Source of O( <sup>1</sup> D)	$\lambda$ (Å)	Excess energy (kcal/mole <sup>a</sup> )	$k_{17}/k_{16}$	Reference
$O_3 + h\nu \rightarrow O(^1D) + O(^3P)$	1470	0 <sup>b</sup>	0.35	Lowenstein <sup>65</sup>
$NO_2 + h\nu \rightarrow NO + O(^1D)$	2288	5.2	0.24	Preston and Cvetanović <sup>66</sup>
$O_2 + h\nu \rightarrow O(^1D) + O(^3P)$	1470	<15 <sup>c</sup>	0.21, 0.26	Young <i>et al.</i> <sup>10</sup>
$O_2 + h\nu \rightarrow O(^1D) + O(^3P)$	1470	15	0.067	Warneck and Sullivan <sup>67</sup>
$O_2 + h\nu \rightarrow O(^1D) + O(^3P)$	1470	15	30	Noxon <sup>29</sup>
$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$	2880	21	0.17	This work
$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$	2537	28	0.28	This work
$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$	2537	28	0.23	DeMore <sup>68</sup>
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	2139	31	0.31	Paraskevopoulos and Cvetanović <sup>12</sup>
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	2139	31	0.29	Yamazaki <sup>69</sup>
$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$	2288	37	0.21	This work
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	1849	45	0.26	Yamazaki and Cvetanović <sup>27, 60</sup>

<sup>a</sup> Maximum possible translational energy in O(<sup>1</sup>D).

<sup>b</sup> Excess He added as a buffer gas.

<sup>c</sup> Ar added to partially buffer gas mixture.

There appears to be no direct measurement of  $k_{16}/k_3$ . However, there are many studies from which  $k_{17}/k_{16}$  can be deduced, and these results are listed in Table IV. Except for two values obtained in the photolysis of O<sub>2</sub> at 1470 Å, all the other values lie between 0.17 and 0.35 even though the experimental conditions and the translational energy of O(<sup>1</sup>D) was considerably different in the different experiments.

## PHOTOLYSIS OF WET OZONE

### Results

We measured  $-\Phi\{O_3\}$  in the presence of H<sub>2</sub>O under different conditions of pressure, wavelength, and light intensity. In these experiments all quantum yields



were based on  $-\Phi_{\infty}\{O_3\} = 4.0$  in excess  $CO_2$  in the absence of  $H_2O$ . The data are in Table V. For a number of experiments a third gas, either  $CO_2$  or He, was added, either after determining  $-\Phi\{O_3\}$  or in a separate experiment, and the quantum yield of  $O_3$  disappearance (designated  $-\Phi'\{O_3\}$ ) again measured. Those experiments in which the third gas was added after the original determination gave the same results as when a fresh unphotolyzed mixture was used. The advantage of a fresh mixture is that no  $O_2$  is present, but the advantage of adding the third gas after the original photolysis is that a direct comparison of the change in  $-\Phi\{O_3\}$  can be made.

The most obvious effect is that  $-\Phi\{O_3\}$  increases with the ratio  $[H_2O]/[O_3]$ , reaching a maximum value of about 19 at  $[H_2O]/[O_3] \sim 2$  and  $[O_3] = 1.1$  Torr. Further increases in  $[H_2O]/[O_3]$  cause a drop in  $-\Phi\{O_3\}$ . This effect is most easily seen in Fig. 7 in which  $-\Phi\{O_3\}$  is plotted vs.  $[H_2O]^{1/2}$  for runs at  $2800 \text{ \AA}$  with  $I_a = 3 \text{ mTorr/min}$  and  $[O_3] = 1.1$  Torr. At low  $H_2O$  vapor pressures  $-\Phi\{O_3\}$  increases linearly with  $[H_2O]^{1/2}$  in agreement with the observations of Forbes and Heidt<sup>2</sup>. A maximum value of about 18 is reached at  $[H_2O]^{1/2} = 1.5 \text{ Torr}^{1/2}$ , and then  $-\Phi\{O_3\}$  falls slightly with further increases in  $[H_2O]$ .

The maximum value of  $-\Phi\{O_3\}$  also seems to increase with  $[O_3]$ , at least at lower  $O_3$  pressures, but this effect is not very marked, perhaps because  $[O_3]$  was only varied by a factor of 10.

The effect of  $I_a$  on  $-\Phi\{O_3\}$  was studied at  $2537 \text{ \AA}$ ,  $[O_3] = 0.18$  Torr, and  $[H_2O]/[O_3] = 2.0$ . A 60-fold drop in  $I_a$  raises  $-\Phi\{O_3\}$  from 4.9 to 9.7, again in

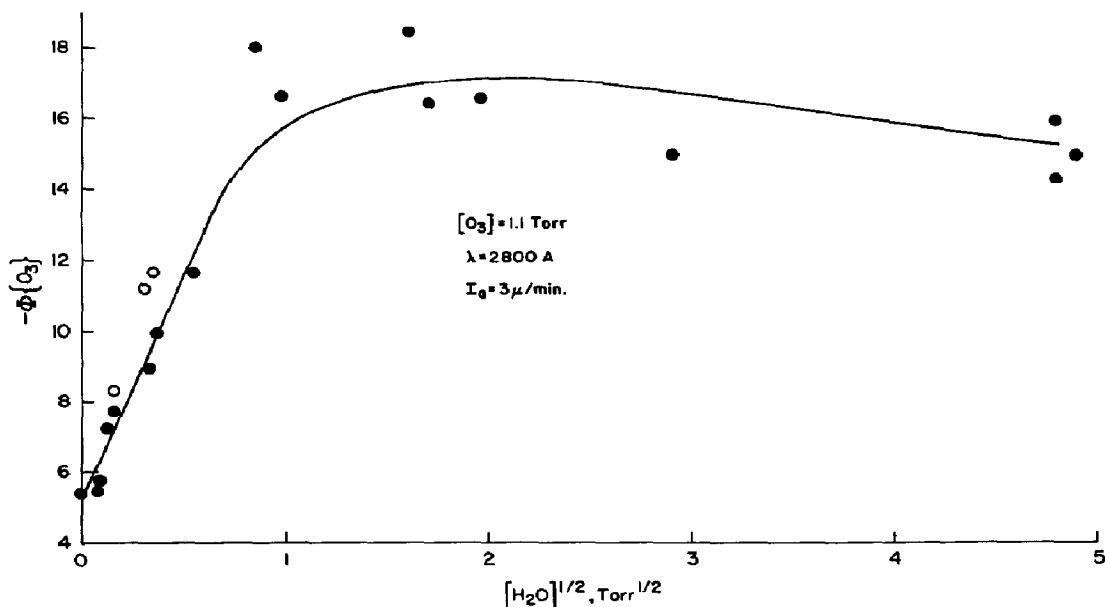


Fig. 7. Plot of the quantum yield of ozone consumption vs.  $[H_2O]^{1/2}$  in the photolysis of wet ozone for short conversions at  $2800 \text{ \AA}$ ,  $25^\circ\text{C}$ ,  $[O_3] = 1.1$  Torr and  $I_a = 3 \text{ mTorr/min}$ . Open circles are for runs with 60–105 Torr of He also present.

accord with the findings of Forbes and Heidt<sup>2</sup>. The results appear to be similar at all wavelengths, and the addition of excess He only raised  $-\Phi\{\text{O}_3\}$  slightly.

The effect of adding  $\text{CO}_2$  is to repress  $-\Phi\{\text{O}_3\}$ , and eventually drop it to 4.0. However, the  $[\text{CO}_2]/[\text{H}_2\text{O}]$  ratio needed to reduce the chain component of  $-\Phi\{\text{O}_3\}$  (*i.e.*  $-\Phi\{\text{O}_3\} - 4.0$ ) to one-half its value is much greater than the  $[\text{CO}_2]/[\text{O}_3]$  ratio necessary to produce the same effect when  $\text{H}_2\text{O}$  is omitted.

Finally one experiment was done with  $\text{H}_2$  instead of water vapor. The conditions were 0.18 Torr  $\text{O}_3$ , 12 Torr  $\text{H}_2$ ,  $\lambda = 2537 \text{ \AA}$ , and  $I_a = 13 \text{ mTorr/min}$ . The quantum yield of  $\text{O}_3$  disappearance was 103, which agrees with the large quantum yields found by others<sup>41,46</sup>, though our value is considerably larger.

One explanation for the discrepancy between the low-intensity steady illumination data and the high-intensity flash photolysis data is that  $\text{H}_2\text{O}_2$  is formed and it initiates the chain step in the low intensity experiments<sup>49</sup>. To check this possibility we carefully looked for induction periods in our  $\text{O}_3$  decay curves. Our results show no induction times, the slopes of the decay curves being independent of conversion even at conversions lower than 0.5%. In a typical run (0.5 Torr  $\text{H}_2\text{O}$ , 0.5 Torr  $\text{O}_3$ ,  $-\Phi\{\text{O}_3\} = 20$ ), the total  $\text{H}_2\text{O}_2$  produced must be  $< 2 \times 10^{-4}$  Torr at 0.5% conversion. It is difficult to believe that this small amount of  $\text{H}_2\text{O}_2$  could successfully compete with  $\text{H}_2\text{O}$  for the  $\text{O}(^1\text{D})$  atom to initiate the chains when 12 Torr of  $\text{H}_2$  produces chain lengths of only 130 or less.

### Mechanism

In the presence of water vapor, the  $\text{O}(^1\text{D})$  atom can react with  $\text{H}_2\text{O}$ :

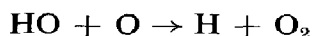


where  $\text{HO}^\pm$  is vibrationally excited HO with sufficient energy ( $\nu \geq 2$ ) to initiate the chain:



In reaction (9b) there is sufficient energy to produce HO ( $\nu = 2$ ) and if the excess translational energy of the  $\text{O}(^1\text{D})$  atom is considered, even HO ( $\nu = 3$ ). The HO radical with  $\nu = 2$  has been observed by Basco and Norrish<sup>43</sup>. In reaction (13) the HO radical produced can have  $\nu \leq 9$ . The reactivity of  $\text{HO}^\pm$  probably depends on its vibrational energy. However, for simplicity we shall assume that for  $\nu \geq 2$ , all the  $\text{HO}^\pm$  are indistinguishable.

The chain-initiation step important in the presence of large concentrations of O atoms:

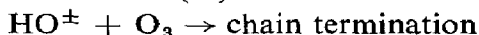
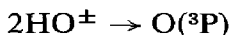


cannot be important here, as pointed out by DeMore<sup>44</sup>. Also in the flash photolysis, where the O atom concentration is even higher, the water-induced chain does not occur<sup>48,49</sup>. We have attempted to fit several mechanisms utilizing the above reaction as a chain initiator, but each has led to a rate law inconsistent with our observations in one way or another.

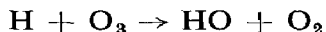
The radical removal steps are:



A number of possible chain-terminating reactions have been omitted for the following reasons. The excited radical  $\text{HO}^\pm$  might have been removed by:



The former reaction undoubtedly occurs, but since  $[\text{HO}^\pm] \ll [\text{HO}]$ , it is negligible compared to reaction (19). The latter reaction is only a formalism, since for kinetic purposes  $\text{HO}^\pm$  is defined as only those HO radicals that produce H atoms when interacting with  $\text{O}_3$  (all the HO radicals with  $\nu \geq 2$  may not be  $\text{HO}^\pm$ ). Wall deactivation steps have been omitted since they must be diffusion controlled, and the addition of excess He only introduces a slight increase in  $-\Phi\{\text{O}_3\}$ . Some wall deactivation may be occurring, but it cannot be the dominant chain-termination step. The possibility that the H atom reacts with  $\text{O}_3$  to terminate the chain, *viz*:



has also been ignored. It cannot be the major chain-termination step, since it would lead to a rate law in which  $-\Phi\{\text{O}_3\}$  would decrease with an increase in  $[\text{O}_3]$ , contrary to our findings.

The mechanism consisting of reactions (1a), (2)–(4), (5b), (9a), (9b), (12), (13) and (18)–(20) leads to the rate law:

$$-\Phi\{\text{O}_3\} = 3 + \alpha + (2k_{3a} + k_{3b})[\text{O}_3]/(k_3[\text{O}_3] + k_9[\text{H}_2\text{O}]) + \frac{2(k_{9b}/k_9)k_{12}[\text{O}_3]\beta}{k_{19}(I_a\beta/k_{18})^{1/2} + k_{20}[\text{H}_2\text{O}]} \quad (\text{II})$$

where

$$\alpha \equiv (k_{3a}[\text{O}_3] + k_9[\text{H}_2\text{O}])/(k_3[\text{O}_3] + k_9[\text{H}_2\text{O}]) \quad (\text{III})$$

and

$$\beta \equiv k_9[\text{H}_2\text{O}]/(k_3[\text{O}_3] + k_9[\text{H}_2\text{O}]) \quad (\text{IV})$$

In deriving the rate law (II), it was assumed that  $[\text{HO}^\pm] \ll [\text{HO}]$ , so that reactions (9b) and (19) do not significantly influence the steady-state value of  $[\text{HO}]$ . The quantity  $\alpha$  varies between 0.75 and 1.0, and is essentially a constant.

The last term in eqn. (II) is the dominant one in determining the change in  $-\Phi\{O_3\}$  when  $H_2O$  is added. At low  $H_2O$  pressures,  $k_{20}[H_2O] < k_{19}(I_a\beta/k_{18})^{1/2}$ , and this term reduces to:

$$\frac{2k_{9b}k_{12}[O_3]}{k_9k_{19}} \left[ \frac{k_9k_{18}[H_2O]}{I_a(k_3[O_3] + k_9[H_2O])} \right]^{1/2}$$

This expression predicts that the increase in  $-\Phi\{O_3\}$  will be inversely proportional to  $I_a^{1/2}$ ; directly proportional to  $([H_2O][O_3])^{1/2}$  at low values of  $[H_2O]/[O_3]$ ; and directly proportional to  $[O_3]$ , but independent of  $[H_2O]$ , at high  $[H_2O]/[O_3]$ . At high  $H_2O$  pressures,  $k_{20}[H_2O]$  is no longer negligible, and an increase in  $[H_2O]$  reduces  $-\Phi\{O_3\}$ . All of these predictions conform to our findings and to the observation that no measurable chain occurs in the flash photolysis, where  $I_a$  is very large.

Though the mechanism leads to a complex rate law, some rate constant ratios can be estimated. For example when  $-\Phi\{O_3\}$  has achieved 1/2 of its increase in Fig. 7 (*i.e.*  $-\Phi\{O_3\} = 12$ ), then  $k_3[O_3] = k_9[H_2O]$ . Thus  $k_9/k_3 \simeq 1.5$ . This value is more than three times larger than found by Biedenkapp *et al.*<sup>48</sup>. However, when combined with our value of  $k_{16}/k_3$  at 2537 Å, it gives  $k_9/k_{16} = 3.0$  in very good agreement with the value of 2.76 found for  $k_9/k_{16}$  by Scott and Cvetanović<sup>38</sup>.

Under most of our conditions reaction (20) is unimportant. In fact it is only of significance at all for the high  $H_2O$  vapor pressures in Fig. 7. With  $[H_2O] = 24$  Torr,  $[O_3] = 1.1$  Torr, and  $I_a = 3$  mTorr/min, then  $-\Phi\{O_3\} = 16$ , a reduction of about 2.5 from its maximum value. Thus for these conditions  $k_{20}[H_2O] \simeq (2.5/12)k_{19}(I_a/k_{18})^{1/2}$ . This leads to  $k_{18}^{1/2}k_{20}/k_{19} = 9.1 \times 10^{-3} M^{-1/2} \text{ sec}^{-1}$ . The best value<sup>61</sup> for  $k_{18}$  is  $1.55 \times 10^9 M^{-1} \text{ sec}^{-1}$ . Since  $k_{19}$  cannot be more than 300 times larger (and probably no more than 10 times larger) than  $k_{18}$ ,  $k_{20} < 10^5 M^{-1} \text{ sec}^{-1}$  and probably  $< 3 \times 10^3 M^{-1} \text{ sec}^{-1}$ . This is a small rate constant for vibrational energy removal, corresponding to  $10^6$ – $10^8$  collisions for deactivation.

The inefficiency of  $H_2O$  in deactivating  $HO^\pm$  appears to be in marked contrast to the results of Kaufman<sup>45</sup>, who studied the H atom– $NO_2$  reaction to produce  $HO^\pm$  and found that the addition of  $H_2O$  vapor upstream of the  $O_3$  inlet could eliminate the reaction of  $HO^\pm$  with  $O_3$ . He did not report his experimental conditions, so that it is not clear how efficient the reaction was. However, for typical flow tube conditions ( $[H_2O] = 1.0$  Torr, flow velocity = 100 cm/sec, displacement between  $H_2O$  and  $O_3$  inlets = 100 cm) the number of collisions with  $H_2O$  would be  $\sim 10^7$  before reaching the  $O_3$  inlet.

A more detailed comparison can be made with the observation of Biedenkapp *et al.*<sup>48</sup>. They found that  $HO(\nu = 1)$  was not quenched by 0.05 torr  $H_2O$  vapor in 20  $\mu\text{sec}$  (100 collisions), but that it was quenched in 150  $\mu\text{sec}$  (700 collisions). If  $HO(\nu = 2)$  behaves similarly to  $HO(\nu = 1)$ , then there is a discrepancy between the two sets of data. Of course it is possible that because of anharmonicity, the match in vibrational levels between  $HO$  and  $H_2O$  is poorer with  $\nu = 2$  or 3

than with  $\nu = 1$ , and that the efficiency of deactivating these levels is less than for  $\nu = 1$ .

If reaction (20) is ignored, eqn. (II) simplifies to:

$$-\Phi_c\{O_3\} = 2(k_{9b}/k_9)(k_{12}/k_{19})k_{18}^{1/2} [O_3] (\beta/I_a)^{1/2} \quad (V)$$

where

$$-\Phi_c\{O_3\} \equiv -\Phi\{O_3\} - 3 - \alpha - \frac{(2k_{3a} + k_{3b}) [O_3]}{k_3 [O_3] + k_9[H_2O]} \quad (VI)$$

With the values of  $k_{3a}/k_3 = 0.75$  and  $k_9/k_3 = 1.5$ ,  $\Phi_c\{O_3\}$  and  $\beta$  can be computed. This has been done for the appropriate data in Table V, and a log-log plot is shown in Fig. 8.

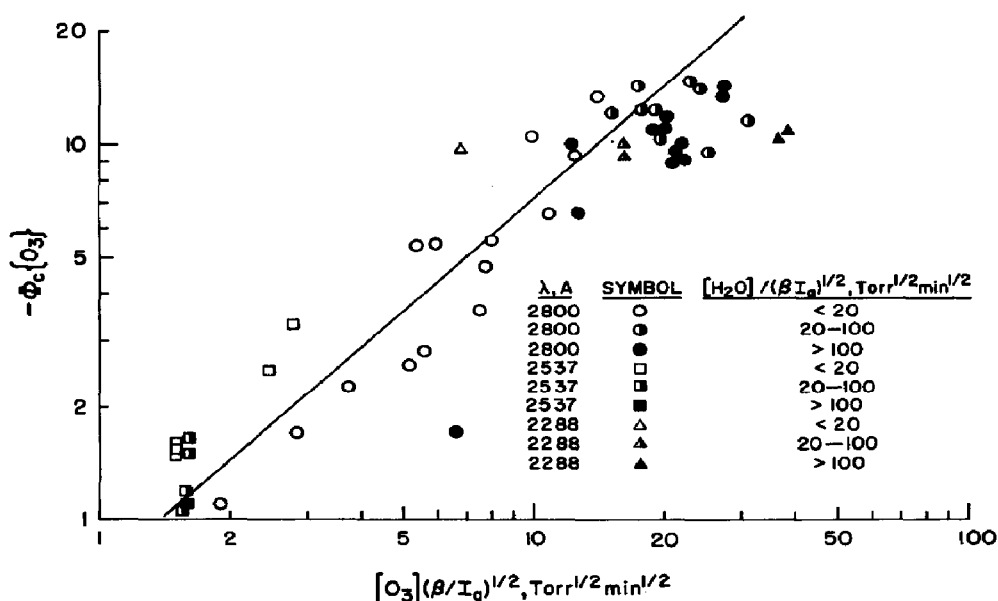


Fig. 8. Log-log plot of the water-chain component of the quantum yield of ozone consumption vs.  $[O_3](\beta/I_a)^{1/2}$  in the photolysis of wet ozone at 25°C.

The data points in Fig. 8 are badly scattered, but a straight line of slope one is drawn to fit the data. Its intercept of  $0.72 \text{ Torr}^{-1/2} \text{ min}^{-1/2}$  is the value of  $(k_{9b}/k_9)(k_{12}/k_{19})k_{18}^{1/2}$ . This corresponds to a value of  $12.7 \text{ M}^{-1/2} \text{ sec}^{-1/2}$ . Since the best value<sup>61</sup> for  $k_{18}$  is  $1.55 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ , and  $k_{12}$  is almost surely smaller than  $k_{19}$ , then  $k_{9b}/k_9 > 3 \times 10^{-4}$ .

In spite of the scatter of the data in Fig. 8, there are some trends which are apparent. The data points at 2800 Å generally lie below those at the lower wavelengths. This suggests that the translational energy in the  $O(^1D)$  atom may affect the value of  $k_{9b}/k_9$ ; the more energy, the higher the value. In fact one would expect this to be the case.

TABLE V  
PHOTOLYSIS OF WET OZONE

[H <sub>2</sub> O] (Torr)	<i>I</i> <sub>a</sub> (mTorr/min)	$-\Phi\{O_3\}$	[CO <sub>2</sub> ] (Torr)	$-\Phi'\{O_3\}$
$\lambda = 2800 \text{ \AA}, [O_3] = 0.20 \text{ Torr}$				
0.195	0.90	7.2		
11.6	0.90	5.7		
$\lambda = 2800 \text{ \AA}, [O_3] = 0.60 \text{ Torr}$				
0	2.2	5.7		
0.25	2.2	10.5		
0.6	2.2	15		
5.2	2.2	14		
20	2.2	10.5		
$\lambda = 2800 \text{ \AA}, [O_3] = 1.1 \text{ Torr}$				
0.0	3.0	5.4		
0.006	3.0	5.4		
0.008	3.0	5.7		
0.013	3.0	7.2		
0.026	3.0	7.7	105 <sup>a</sup>	8.3
0.116	3.0	8.9	60 <sup>a</sup>	11.7
0.12	3.0	—	90 <sup>a</sup>	11.2
0.13	3.0	10		
0.3	3.0	11.6	24	6.5
0.7	3.0	18		
0.97	3.0	16.7		
2.5	3.0	18.5		
3.0	3.0	16.5		
3.8	3.0	16.6	25	11.6
8.0	3.0	15		
22	3.0	16		
23	3.0	14.3		
24	3.0	15		
$\lambda = 2800 \text{ \AA}, [O_3] = 1.3 \text{ Torr}$				
0.010	3.4	6.6		
0.019	3.4	8.8	20	4.0
0.067	3.4	10.8		
7.1	3.4	13.8		
8.2	3.4	13.2		
20	3.4	14.1		
22	3.4	13.2		
$\lambda = 2800 \text{ \AA}, [O_3] = 1.7 \text{ Torr}$				
0.0	3.7	5.6		
0.05	3.7	8.2	20	5.0
0.28	3.7	14.5		
1.05	3.7	15.0	26	9.5
2.3	3.7	19	26	11
3.4	3.7	18.4		
5.3	3.7	13.8	24	11.9
21.3	3.7	18.4		
21.5	3.7	18		
$\lambda = 2800 \text{ \AA}, [O_3] = 6.0 \text{ Torr}$				
0.52	4.0	16.5	22	6.5

Table V cont.

[H <sub>2</sub> O] (Torr)	<i>I<sub>a</sub></i> (mTorr/min)	$-\Phi\{\text{O}_3\}$	[CO <sub>2</sub> ] (Torr)	$-\Phi'\{\text{O}_3\}$
$\lambda = 2537 \text{ \AA}, [\text{O}_3] = 0.18 \text{ Torr}$				
0.0	13	5.4		
0.0	13	5.5		
<0.1	13	5.5		
0.39	53	4.9		
0.39	25	4.8		
0.39	4.2	6.85		
0.39	0.87	9.7		
0.43	13	5.3		
0.67	13	5.5		
0.95	13	5.7	8.5	5.1
1.06	13	—	25 <sup>a</sup>	5.5
1.07	13	5.7	12	5.5
1.7	13	5.7		
1.8	13	5.3		
2.0	13	5.5	15	5.15
2.4	13	5.5	14.5	4.9
3.5	13	5.3		
7.7	13	5.1		
8.5	13	5.7		
9.3	13	5.5		
12.4	13	5.1		
16.4	13	5.2		
16.4	13	5.2		
$\lambda = 2288 \text{ \AA}, [\text{O}_3] = 1.1 \text{ Torr}$				
0.90	4.4	14.4		
2.2	3.6	14.4		
2.7	3.6	13.6		
4.9	0.8	14.5		
20	0.8	15.0		

<sup>a</sup> He rather than CO<sub>2</sub> added.

It is also clear from the data that the points for values of  $[\text{H}_2\text{O}]/(\beta I_a)^{1/2} > 100 \text{ Torr}^{-1/2} \text{ min}^{-1/2}$  lie lower than those for  $[\text{H}_2\text{O}]/(\beta I_a)^{1/2} < 20 \text{ Torr}^{-1/2} \text{ min}^{-1/2}$ . At the higher values of the parameter, reaction (20) is playing some role, being about 30% as important as reaction (19) as a deactivating step. Thus the ratio  $k_{18}^{1/2} k_{20}/k_{19}$  is about  $0.02 \text{ M}^{-1/2} \text{ sec}^{-1/2}$  in reasonable agreement with our previous estimate. A summary of the pertinent rate constant ratios is given in Table VI.

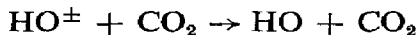
It is now apparent why in some experiments the water-chain seems to vary inversely with  $I_a^{1/2}$ , whereas in others it is nearly independent of  $I_a$ . For different conditions the termination may be either by radical-radical steps or by deactivation of HO<sup>±</sup> by H<sub>2</sub>O.

#### CO<sub>2</sub> present

With CO<sub>2</sub> present there are two possible additional reactions. One of these is:



The other is the quenching of  $\text{HO}^\pm$ :



From our results there is no evidence that the deactivating reaction is important, and we shall neglect it. Then the mechanism predicts that:

$$-\Phi'(\text{O}_3) = 3 + \alpha' + \frac{(2k_{3a} + k_{3b}) [\text{O}_3]/(k_3[\text{O}_3] + k_9[\text{H}_2\text{O}] + k_{16}[\text{CO}_2]) + 2(k_{9b}/k_9) k_{12}[\text{O}_3] \beta'}{k_{19}(I_a\beta'/k_{18})^{1/2} + k_{20}[\text{H}_2\text{O}]} \quad (\text{VII})$$

where

$$\alpha' \equiv (k_{3a}[\text{O}_3] + k_9[\text{H}_2\text{O}] + k_{16}[\text{CO}_2]) / (k_3[\text{O}_3] + k_9[\text{H}_2\text{O}] + k_{16}[\text{CO}_2]) \quad (\text{VIII})$$

and

$$\beta' \equiv k_9[\text{H}_2\text{O}] / (k_2[\text{O}_3] + k_9[\text{H}_2\text{O}] + k_{16}[\text{CO}_2]) \quad (\text{IX})$$

If reaction (20) is ignored, a comparison of the rate expression in the absence and presence of  $\text{CO}_2$  leads to the simple result:

$$(\Phi_c(\text{O}_3)/\Phi'_c(\text{O}_3))^2 = 1 + \frac{k_{16}[\text{CO}_2]}{k_9([\text{H}_2\text{O}] + k_3[\text{O}_3]/k_9)} \quad (\text{X})$$

where

$$-\Phi'_c(\text{O}_3) \equiv -\Phi_c(\text{O}_3) - 3 - \alpha' - \frac{(2k_{3a} + k_{3b})[\text{O}_3]}{(k_3[\text{O}_3] + k_9[\text{H}_2\text{O}] + k_{16}[\text{CO}_2])}$$

Both  $-\Phi_c(\text{O}_3)$  and  $-\Phi'_c(\text{O}_3)$  can be computed using  $k_{3a}/k_3 = 0.75$ ,  $k_3/k_9 = 0.67$  and  $k_{16}/k_9 = 0.33$ . Likewise  $[\text{CO}_2]/([\text{H}_2\text{O}] + k_3[\text{O}_3]/k_9)$  can be computed. The appropriate plot is shown in Fig. 9.

The data points in Fig. 9 are extremely badly scattered. This occurs because both  $\Phi_c(\text{O}_3)$  and  $\Phi'_c(\text{O}_3)$  are computed as the differences between numbers which are often similar. The uncertainty is compounded when the ratio is taken, and even

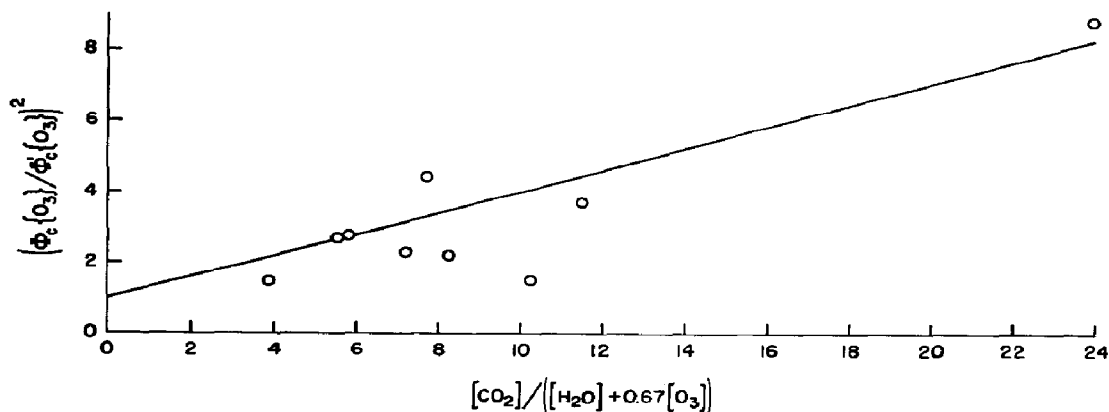


Fig. 9. Plot of  $(\Phi_c(\text{O}_3)/\Phi'_c(\text{O}_3))^2$  vs.  $[\text{CO}_2]/([\text{H}_2\text{O}] + 0.67[\text{O}_3])$  in the photolysis of wet ozone in the presence of  $\text{CO}_2$  at  $25^\circ\text{C}$ .



this ratio is squared. Nevertheless, if we force a line with an intercept of unity through the data then the slope of this line, which corresponds to  $k_{10}/k_9$ , is about 0.3 in satisfactory agreement with the value of 0.36 found by Scott and Cveto-  
vič<sup>38</sup>.

Of course the argument can be raised that values of  $k_{10}/k_9$  and  $k_9/k_3$  were assumed and used in computing both coordinates for Fig. 9. However, in most cases only minor corrections resulted from their use, and large errors in the values would not have influenced the outcome significantly. In any case, our results with wet ozone in the presence of  $\text{CO}_2$  are consistent with all of our other results.

#### PHOTOLYSIS OF $\text{O}_3$ - $\text{N}_2\text{O}$ MIXTURES

##### Results

When  $\text{O}_3$  was photolyzed to 1-2% conversion in the presence of  $\text{N}_2\text{O}$ ,  $-\Phi\{\text{O}_3\}$  dropped, reaching about 4. The data at the three wavelengths are shown in Figs. 10 and 11. For these experiments, the quantum yields are based on absolute actinometry and not on  $-\Phi_\infty\{\text{O}_3\}$  in the presence of  $\text{CO}_2$ . The values of  $-\Phi_\infty\{\text{O}_3\}$  for  $\text{N}_2\text{O}$  are listed in Table I, and they are virtually identical to those with  $\text{CO}_2$  and  $\text{N}_2$ .

The results at 2800 and 2288 Å are shown in Fig. 10. The half-quenching ratio is about 1.5 at 2800 and about 4.0 at 2288 Å. Though the scatter in each set of data is considerable, there is no doubt that there is a wavelength effect. The quenching can be associated with the competition between reaction (3) and reaction (21):



The wavelength effect reflects the influence of excess translational energy in the  $\text{O}(^1\text{D})$  atom. At the half-quenching point  $k_3[\text{O}_3] = k_{21}[\text{N}_2\text{O}]$ , so that the half-quenching ratio equals  $k_3/k_{21}$ . Our results agree with those of Goldman *et al.*<sup>52</sup>

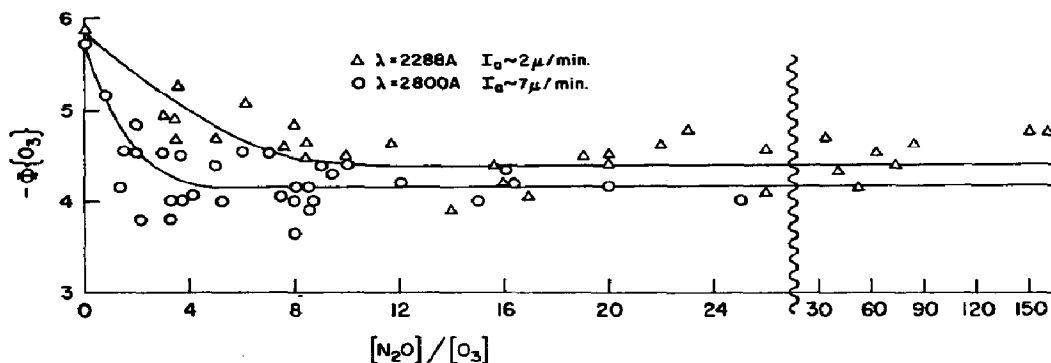


Fig. 10. Plot of the quantum yield of  $\text{O}_3$  consumption vs.  $[\text{N}_2\text{O}]/[\text{O}_3]$  in the photolysis of  $\text{O}_3$ - $\text{N}_2\text{O}$  mixtures for 1-2% conversions at  $25^\circ\text{C}$  and  $[\text{O}_3] \sim 0.9$  Torr. Note break in abscissa and change of scale at  $[\text{N}_2\text{O}]/[\text{O}_3] = 27$ .

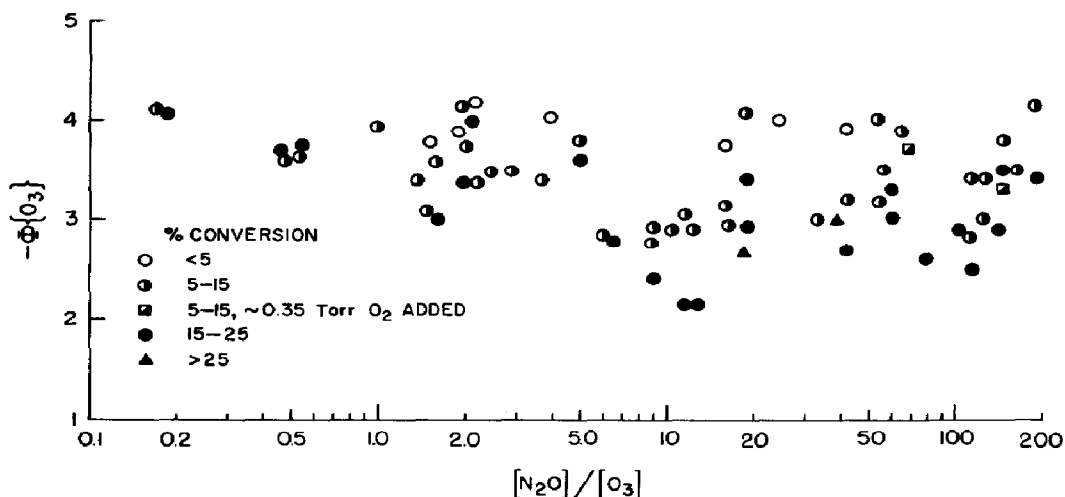


Fig. 11. Semi-log plot of the quantum yield of  $O_3$  consumption vs.  $[N_2O]/[O_3]$  in the photolysis of  $O_3-N_2O$  mixtures for various conversions at  $2537 \text{ \AA}$ ,  $25^\circ\text{C}$ ,  $[O_3] = 0.18 \text{ Torr}$  and  $I_a = 3-30 \text{ mTorr/min}$ .

TABLE VI

SOME RATE CONSTANT RATIOS

Ratio	Value	Units	Source
$k_{3a}/k_{3b}$	3.0	None	—
$k_{18}^{1/2} k_{20}/k_{19}$	0.02	$M^{-1/2} \text{ sec}^{-1/2}$	Fig. 8
$\frac{k_{9a}/k_{12}k_{18}^{1/2}}{k_9k_{19}}$	12.7	$M^{-1/2} \text{ sec}^{-1/2}$	Eqn. (V), Fig. 8

who photolyzed  $O_3$  in the presence of  $N_2O$  at  $2537$  and  $2288 \text{ \AA}$  and measured the  $N_2$  yield rather than the  $O_3$  decay. They found  $k_3/k_{21} = 2.6$  at  $2537 \text{ \AA}$ , which is intermediate to our two values, and  $k_3/k_{21} = 4.1$  at  $2288 \text{ \AA}$  in excellent agreement with our value.

At  $2537 \text{ \AA}$ , we do not have good half-quenching measurements, but data were taken for various conversions and absorbed intensities. The results are shown in Fig. 11.  $I_a$  was varied from 3 to 30 mTorr/min, but this had no effect on the results. However, a noticeable effect was observed with increases in percentage conversion. As the percentage of  $O_3$  converted increased,  $-\Phi_{\infty}\{O_3\}$  dropped, reaching about  $2.8 \pm 0.6$  at our most extended conversions. It is interesting to note that the  $[N_2O]/[O_3]$  ratio is about 2-3 which reduces  $-\Phi\{O_3\}$  half way between its values of 4.1 at low ratios and 2.8 at high ratios. This should correspond to  $k_3/k_{21}$  at  $2537 \text{ \AA}$ , and the value of 2-3 is consistent with that of Goldman *et al.*<sup>52</sup>

The drop in  $-\Phi\{O_3\}$  at longer conversions might have been attributed to reaction (7) which could become important as  $O_2$  accumulates. Actually this is not the case, as shown by two experiments at 5-15% conversion in which 0.35 Torr of  $O_2$  was added initially. This amount of  $O_2$  is more than would have been produced by complete conversion of the 0.18 Torr of  $O_3$ . Yet the results with  $O_2$

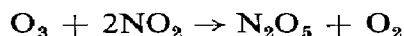
added are no different than with  $O_2$  absent for the same conversion, *i.e.*  $-\Phi\{O_3\}$  is larger than for higher conversions.

The reason why reaction (7) is unimportant in this system is because  $NO_2$  is produced as a product. (Even though the  $NO_2$  further reacts with  $O_3$  to produce  $N_2O_5$ , an equilibrium is established, and some  $NO_2$  is present.) The rate constant for the  $O(^3P) + NO_2$  reaction is  $3.6 \times 10^9 M^{-1} sec^{-1}$  at room temperature<sup>62</sup> whereas that for reaction (7) is  $2 \times 10^8 M^{-2} sec^{-1}$  for  $N_2$  as a chaperone<sup>63</sup>. With  $N_2O$  as a chaperone, the rate constant is probably somewhat larger. With 20 Torr  $N_2O$  the  $O(^3P) + NO_2$  reaction will be more important than reaction (7) for  $[NO_2]/[O_2] > 10^{-4}$ . Since  $[NO_2]$  almost surely reaches a value of  $> 10^{-4}$  Torr very quickly and since  $[O_2] = 0.35$  Torr, reaction (7) is never significant in this system.

Another possible explanation for the low values of  $-\Phi\{O_3\}$  at high conversions could be an experimental artifact due to optical absorption of one of the products,  $NO_2$  or  $N_2O_5$ , both of which absorb radiation at 2537 Å. To check this possibility, mixtures of  $NO$  and  $O_3$  were reacted. When small amounts of  $NO$  were added to excess  $O_3$ , the optical absorption dropped immediately to a value expected from  $O_3$  alone for the overall stoichiometric reaction:



When the stoichiometric amount of  $NO$  was used, the light absorption dropped practically to zero. These experiments were repeated with 50%  $NO_2$  diluted in  $O_2$  replacing the  $NO$ , and identical results were obtained based on the stoichiometric relation:



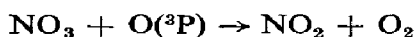
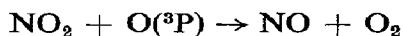
The  $O_3$  removal rate was consistent with the known rate constant<sup>64</sup>, (reaction complete in  $< 6$  sec). It is clear that the extinction coefficients of both  $NO_2$  and  $N_2O_5$  are sufficiently smaller than that of  $O_3$ , so that these molecules do not interfere with the optical analysis for  $O_3$  decay.

### Mechanism

In addition to the steps in the pure  $O_3$  system, reactions (1a) and (2)–(5) the following reactions are important in the presence of  $N_2O$ :



There are other reactions that also occur. For example the  $O(^3P)$  atom may be removed by  $NO_2$  or  $NO_3$  rather than  $O_3$ :



However, these reactions are immediately followed by the rapid reactions (22) and (23), respectively, so that kinetically they are indistinguishable from reaction (4). Also NO may react with  $\text{NO}_3$ :



Again this reaction followed by reaction (23) is kinetically indistinguishable from reaction (22) followed by reaction (23), and can also be ignored (or included).

Other reactions that can be envisioned are unimportant. Deactivation of  $\text{O}_2({}^1\Delta)$  by  $\text{N}_2\text{O}$  is much too slow to play any role<sup>65</sup>. The reaction of  $2\text{NO}_3$  molecules is also too slow ( $k = 3.7 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ )<sup>66</sup> to compete with the rapid reaction of NO with  $\text{NO}_3$  ( $k = 3-6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ )<sup>66</sup>.

The rate constant ratio  $k_{21a}/k_{21}$  has been shown to be  $\sim 0.37$ , at least at 2537 and 2288 Å<sup>63</sup>, though a value as high as 0.50 is possible<sup>67</sup>. Under ordinary conditions, the equilibrium in reaction (24) is shifted far to the right,  $K_{24,-24}$  being  $0.8 \times 10^{10} \text{ M}^{-1}$  at 25°C<sup>66</sup>. If this situation prevails, then in excess  $\text{N}_2\text{O}$ , the mechanism predicts that  $-\Phi_\infty\{\text{O}_3\} = 4.9$  for  $k_{21a}/k_{21} = 0.37$ . If  $k_{21a}/k_{21}$  is as large as 0.50, then  $-\Phi_\infty\{\text{O}_3\}$  should be 4.5.

In our system, however, NO is continually being produced and it reacts readily with  $\text{NO}_3$  ( $k = 3-6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ ) at 298 K<sup>66</sup>. Consequently the equilibrium in reaction (24) may be shifted to the left. Computations based on our reaction conditions and the known rate constants indicate that the shift is negligible.

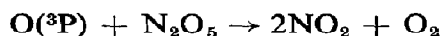
The situation is that  $-\Phi_\infty\{\text{O}_3\}$  should be at least 4.5 and probably 4.9. Under none of our conditions with excess  $\text{N}_2\text{O}$  was such a large value observed. The only explanation is that one of the products must be scavenging  $\text{O}_2({}^1\Delta)$  or  $\text{O}({}^3\text{P})$  in such a way that  $-\Phi\{\text{O}_3\}$  is reduced. This reaction must be efficient, and proceed to a measureable extent even at 1-2% conversion.

The most obvious possibility of a scavenger is  $\text{N}_2\text{O}_5$ , since it and  $\text{O}_2$  are the only major products, and  $\text{O}_2$  has been shown to be inefficient in this system. To test this possibility, we did the following pair of experiments. In one experiment,  $\text{NO}_2$  was reacted with 0.20 Torr of  $\text{O}_3$ , so that 15% of the  $\text{O}_3$  was consumed. 3 Torr of  $\text{CO}_2$  was added which then made a mixture consisting of 3 Torr  $\text{CO}_2$ , 0.17 Torr  $\text{O}_3$ , 0.3 Torr  $\text{N}_2\text{O}_5$  and 0.3 Torr  $\text{O}_2$ . The mixture was then photolyzed and the rate of  $\text{O}_3$  disappearance measured. In the other experiment of the pair, pure  $\text{O}_3$  was photolyzed to 15% conversion, 3 Torr of  $\text{CO}_2$  was added, and then the mixture was photolyzed. In both photolyses the reaction mixtures contained 3 Torr of  $\text{CO}_2$  and 0.17 Torr of  $\text{O}_3$ . However, the former mixture also contained 0.3 Torr each of  $\text{N}_2\text{O}_5$  and  $\text{O}_2$ , whereas the latter contained 0.45 Torr of  $\text{O}_2$  only. This pair of experiments was repeated three times, and in each case the rate of  $\text{O}_3$  disappearance was always 30% lower in the former mixture, in spite of the fact

that there was more  $O_2$  in the latter mixture. It is clear that  $N_2O_5$  deactivates either  $O(^3P)$  or  $O_2(^1\Delta)$ , or both. In the case of  $O(^3P)$  the reaction would have to be:

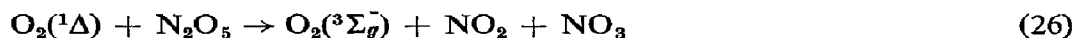


rather than



in order to cause a reduction. (This does not imply that the latter reaction may not occur also.) Both reaction (25) and deactivation of  $O_2(^1\Delta)$  by  $N_2O_5$  lead to the result that in excess  $N_2O$ ,  $-\Phi_\infty\{O_3\}$  should drop to 2.5–2.9 at very large conversions in accordance with our findings at 2537 Å. The relative rate constant for the competition between  $O_3$  and  $N_2O_5$  for either  $O(^3P)$  or  $O_2(^1\Delta)$ , as the case may be, can be estimated to be ~0.8, the reaction with  $N_2O_5$  being slower.

The possibility of deactivation of  $O_2(^1\Delta)$  by  $N_2O_5$  via the dissociative reaction:



is particularly intriguing since the reaction is 2 kcal/mole exothermic.

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