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**A FLASH PHOTOLYSIS-RESONANCE  
FLUORESCENCE STUDY OF THE  
FORMATION OF O(<sup>1</sup>D) IN THE PHOTOLYSIS  
OF WATER AND REACTION OF O(<sup>1</sup>D)  
WITH H<sub>2</sub>, Ar AND He**

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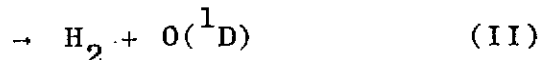
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A FLASH PHOTOLYSIS-RESONANCE FLUORESCENCE STUDY OF THE  
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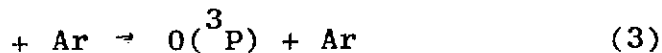
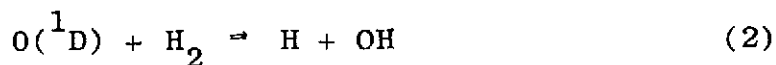
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Abstract

The relative importance of two primary processes in the  
photolysis of water

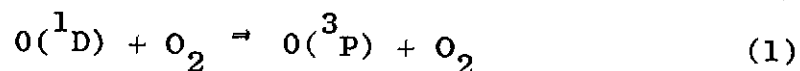


have been determined in a direct manner by time resolved  
detection (via resonance fluorescence) of H and O formed in  
processes I and II respectively. The initially formed  
 $O(^1D)$  was deactivated to ground state  $O(^3P)$  prior to  
detection via resonance fluorescence. The relative quantum  
yields for processes I and II are 0.89 and 0.11 for the  
wavelength interval 105 to 145 nm and  $\geq 0.99$  and  $\leq 0.01$  for  
the wavelength interval 145 to 185 nm. Rate constants at  
 $300^\circ K$  for the reactions



a - NASA/NRC Resident Research Associate, 1972-1974.

have been determined relative to that for



by measuring the increase in H signal or decrease in O signal as

a function of H<sub>2</sub>, Ar or He pressure. Taking  $k_1 = (6 \pm 1) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , we obtain the following results:

$k_2 = (2.5 \pm 1.0) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ,  $k_3 = (8.3 \pm 2.3) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  and  $k_4 < 5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ .

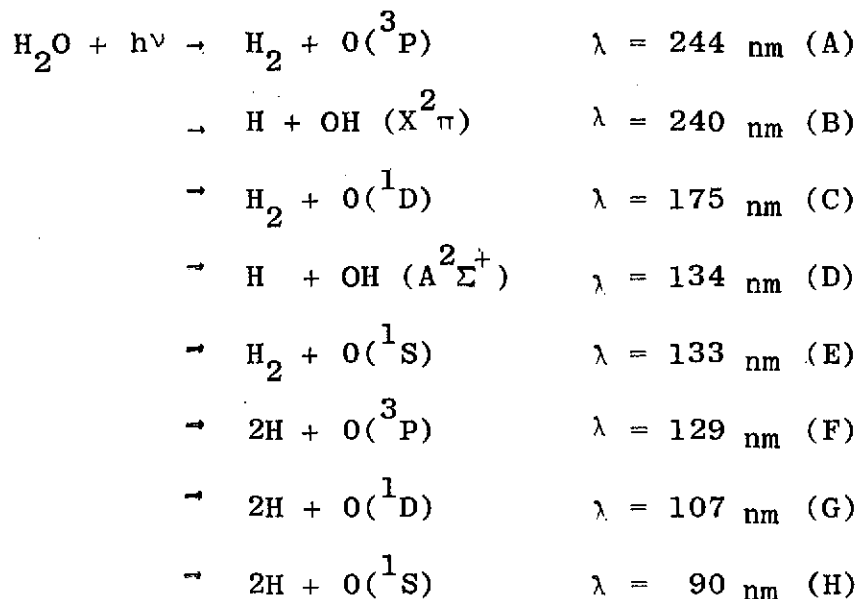
## I. Introduction

The photochemistry of water vapor has been the subject of numerous investigations<sup>1</sup> not only for its intrinsic chemical importance but also for the implications relating to other branches of science. For example, its role in astronomical phenomena is considerable. The emission features in the coma of comets arising from species such as H, OH and O(<sup>1</sup>D) have long been attributed to photodissociation of water vapor<sup>2</sup> evaporating from an icy nucleus.<sup>3</sup> The recent detection<sup>4</sup> of the 1.3 cm microwave transition of water in the coma of Comet Bradfield confirms this view. In addition, water was the second polyatomic molecule detected in interstellar space<sup>5</sup> and photodissociation in the interstellar radiation field determines the lifetime of interstellar water.<sup>6</sup>

Finally, water is a significant minor constituent of the atmospheres of Earth, Venus and Mars.<sup>7</sup> It now appears that products of water photodissociation such as H and OH play a crucial role in maintaining the chemical stability of the CO<sub>2</sub> atmosphere on Mars and Venus.<sup>8</sup>

The following primary processes in the photolysis of water may be considered. The threshold wavelengths ( $\lambda$ ) have been

calculated from the heats of formation given previously.<sup>9</sup>

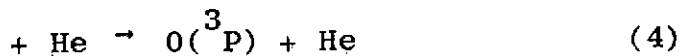
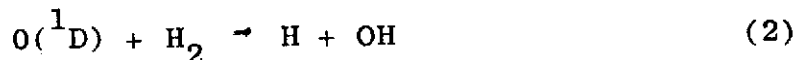


This list may be considerably reduced for reasons given in the following discussion. For example, the use of a LiF window with a cut-off at 105 nm eliminates the importance of process (H) and makes the contribution from process (G) negligible for the 105 to 145 nm range. In addition, we make no distinction between processes (B) and (D) for the purpose of these experiments; formation of OH ( $A{}^2\Sigma^+$ ) has been the subject of several quantitative investigations.<sup>10</sup> The formation of  $\text{O}({}^1\text{S})$  may occur via process (E), but this species goes undetected in these experiments. This follows because any O-atoms formed in an electronically excited state must be deactivated to ground state  $\text{O}({}^3\text{P})$  prior to detection via resonance fluorescence. Using available rate constants<sup>11</sup>

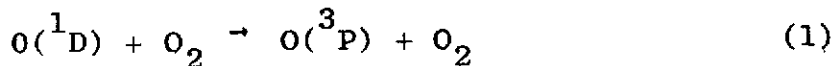
for reaction of  $O(^1S)$  with  $H_2O$  ( $9 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ) and with Ar ( $4 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ), it is clear that under the conditions of the present experiments ( $[Ar] = 10^3 [H_2O]$ ) less than 1% of  $O(^1S)$  formed will be deactivated to  $O(^3P)$  and detected. Although direct formation of  $O(^3P)$  via processes (A) or (F) is not expected to be significant, these processes are included here for the sake of completeness. Other than these two processes, we are left with the major processes  $H_2O + h\nu \rightarrow H + OH$  and  $H_2O + h\nu \rightarrow H_2 + O(^1D)$ .

The relative importance of these two processes has been the subject of several studies, most of which are indirect.<sup>12-18</sup> The present study utilizes a technique for the direct observation of the pertinent species under highly controlled conditions.

Since the accuracy of the method employed here depends on rate constants for several reactions of  $O(^1D)$ , we have measured rate constants for the reactions



relative to that for the reaction<sup>19</sup>



Of particular concern was the possibility of physical

deactivation of  $O(^1D)$  by  $H_2$ <sup>20-23</sup> and the  
wide range of values for  $k_3$ <sup>24-26</sup> and  $k_4$ <sup>27,21,26</sup> that  
appear in the literature.



## II. Experimental

The technique utilizes the vacuum ultraviolet flash photolysis of  $H_2O$  combined with time resolved, simultaneous detection of H and O via resonance fluorescence at 121.6 and 130.2 nm respectively. The apparatus has been described in detail elsewhere.<sup>28</sup> Pressures of reactant and diluent gases were measured to better than  $\pm 1\%$  using Baratron capacitance manometers (0 to 3 torr and 0 to 1000 torr ranges) and a Wallace and Tiernan absolute pressure gauge. The reaction mixtures were prepared and stored in a 22 liter pyrex bulb from which the mixtures were allowed to flow through the reaction vessel at a rate sufficient to replenish the gas between photolyzing pulses. An automatic pressure regulator controlled the total pressure of the gas mixture to better than  $\pm 0.1$  torr.

A spontaneous discharge in flowing nitrogen provided a 200 joule pulse of vacuum ultraviolet radiation approximately 2  $\mu$ sec in width at half-peak-height. The source of both the 121.6 nm Lyman-alpha resonance radiation and the 130.2 nm atomic oxygen radiation was a microwave powered discharge lamp using He as the carrier. Airco 99.9999% He was passed through a liquid  $N_2$  trap and thence through the lamp at about 1 torr pressure.

The atomic resonance radiation generated in the flow lamp is due to impurities (such as water or oxygen), presumably present in the He or picked up in the flow system. This can lead to variations in the relative intensities at the two lines and is particularly significant for a newly installed lamp. All experiments reported here employed a lamp through which helium had been flowed continuously for at least 24 hours. In addition, relative sensitivities of the system for the detection of H and O were determined frequently by a method described in section III.

The H-atom detector and O-atom detector were placed on opposite sides of the reaction vessel and viewed the fluorescence zone at right angles to both photolysis and resonance light beams. Both detectors were EMR 542-G solar blind photomultipliers operated from the same high voltage power supply. The H-atom detector was equipped with a flowing  $O_2$  filter and the O-atom detector had a  $CaF_2$  window interposed between it and the fluorescence zone. These filters effectively eliminated detection of any signal due to O by the H-atom detector and, conversely, any signal due to H by the O-atom detector. This was demonstrated by flashing an  $O_2$ -He mixture and a  $CH_4$ -He mixture and noting the absence of any resonance fluorescence signal in the H-detector and O-detector, respectively.

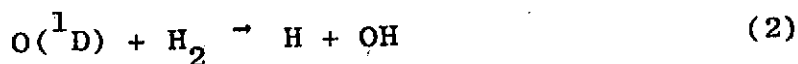
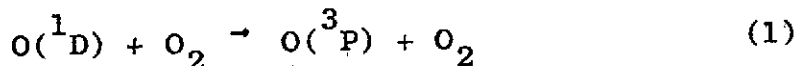
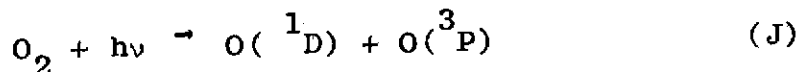
The measurements were made by means of photon counting and multichannel scaling. Signals from both detectors were stored simultaneously in separate halves of the multichannel analyzer. The information of interest in these experiments is the initial signal at zero time since this is directly related to the concentration of the atomic species formed in the photodissociation of  $H_2O$  by the pulse of vacuum UV light. This is in contrast to the more familiar use of such an apparatus to provide kinetic information from the decay of the atomic species. The information stored in the multichannel analyzer was reduced via a time-shared IBM 1800 computer. This operation involved subtracting the average background due to the constant scattered light signal and fitting the logarithm of the experimental atom decay against real time with a linear least-squares program to obtain values for the intercept and the slope. As mentioned above, it was the intercept or signal at  $t = 0$  that was primarily important in these experiments.

The major advantage of simultaneous detection of both H and O is that fluctuations in flash lamp intensity and resonance lamp intensity during the course of one hundred

flashes are largely cancelled since the ratio of H to O signals would not be altered. Phenomena which could effect this ratio are variations in the relative intensities of the 121.6 and 130.2 nm lines in the resonance lamp and variations in window transmission at these two wavelengths due to formation of deposits, F-centering, etc. during the course of the experiment. Possible contributions from these effects were monitored by frequent determination of the relative sensitivities of the total system for H and O by a method which is described in the next section.

### III. Sensitivity of System for H and O.

Consider the following reaction sequence:



It is evident that, in the presence of sufficient  $\text{H}_2$  such that reaction (2) dominates over reaction (1), the concentration of  $\text{O}({}^3\text{P})$  equals the concentration of H. Since both  $\text{O}({}^3\text{P})$  and H disappear by a combination of diffusion and termolecular reaction with  $\text{O}_2$ , time resolved detection is required. At high  $\text{H}_2$  pressures the loss of  $\text{O}({}^1\text{D})$  is dominated by the  $\text{O}({}^1\text{D}) + \text{H}_2$  reaction. For example, with 1 torr of  $\text{H}_2$  in the reaction mixture the decay rate of  $\text{O}({}^1\text{D})$  would be comparable to the flash duration,  $\sim 2 \mu\text{sec}$ . Under these conditions, the H and O signals extrapolated to zero time would correspond to equal H and O concentration and the measured atom signal ratio would give the relative sensitivity of the system for H and O.

There are several corrections to be applied to this argument to make it more exact. In order of decreasing importance they are:

- (a) production of  $\text{O}({}^3\text{P})$  in addition to that from process J. Arguments are presented in section V that under the conditions

of our experiments there is a contribution from the process  $O_2 + h\nu \rightarrow 2O(^3P)$ . The net result is that  $O(^3P)/O(^1D)$ , instead of being unity, is equal to 1.2/0.8.

(b) incomplete interception of  $O(^1D)$  by  $H_2$ . From the result  $k_2/k_1 = 4.23$  (see section V) we calculate that with  $O_2 = 0.5$  torr and  $H_2 = 2.0$  torr as in our calibration experiment, the rate of  $O(^1D) + H_2$  is 17 times that of  $O(^1D) + O_2$ . Thus we overestimate the O signal by about 6% and underestimate the H signal also by 6%. The use of higher pressures of  $H_2$  would have decreased this correction but increased the quenching correction discussed in (c).

(c) quenching of H and O resonance radiation. The data are given in the appendix. These lead to underestimation of the H signal by 6% from  $H_2$  quenching and by 7% from He quenching. The O signal was similarly underestimated by 3% due to He quenching.

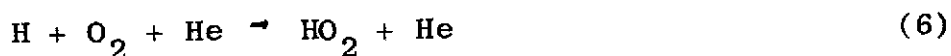
It is clear that while all corrections should be made because of their cumulative importance, correction (a) is by far the most significant.

Table I summarizes the results of the calibration for H and O performed immediately after the water experiments which are reported in the following section. As in the case of the water experiments, signals for H and O were recorded simultaneously. The signal was always observed to decay exponentially with time. The signals given in Table I are the intercepts at  $t = 0$  calculated from a linear least-squares fit of the data.

A possible complication would be the occurrence of the reaction



following the sequence (J), (1), (2). This would yield two H for every O(<sup>1</sup>D) reacting with H<sub>2</sub> and result in an over-estimation of the H sensitivity by a factor of 2. However, using the rate constants<sup>29,30</sup> for reactions (5) and (6),



it is readily shown that the rate of formation of H via reaction (5) is comparable to the rate of removal of H via reaction (6) under the conditions of our experiments.

$$R_5 = 0.7 \times 10^{-14} \times 6.4 \times 10^{16} = 440 \text{ s}^{-1}$$

$$R_6 = 1.6 \times 10^{-32} \times 1.6 \times 10^{16} \times 1.6 \times 10^{18} = 410 \text{ s}^{-1}$$

Thus the H atom signal would deviate considerably from a pure exponential decay and the decay rate would be considerably slower than predicted on the basis of reaction (6) alone. Since we observed good exponential decays of the H signal (both visually on the oscilloscope screen and also as judged by the standard deviation of the least squares fit of the data) and since the observed decay rates were within 10 to 20% of that calculated for reaction (6), we conclude that OH is being removed from the system by some reaction other than reaction (5). If it is reaction with some undetected impurity in the  $H_2$ , it either does not react to form H or else does so on at a rate much faster or much slower than the rate of removal of H via reaction (6).



Table I: Calibration of relative system sensitivity  
for detection of H and O<sup>a</sup>

Detector	Observed Signal <sup>b</sup>	Corrections to observed signal				Corrected Signal	Relative Signal
		Excess <sup>c</sup> O( <sup>3</sup> P)	O( <sup>1</sup> D) Reaction <sup>d</sup>	Resonance H <sub>2</sub>	Quenching <sup>e</sup> He		
H	365	-	÷ 0.94	÷ 0.94	÷ 0.93	444	1.12
O	613	÷ 1.5	÷ 1.06	-	÷ 0.97	398	1.00

a. O<sub>2</sub>:0.5 torr, H<sub>2</sub> = 2.0 torr, He = 50 torr

b. counts/200 μsec, 15 flashes, 70 joules per flash; sapphire window on flash lamp precludes formation of O(<sup>1</sup>S) from O<sub>2</sub> photolysis.

c. see paragraph (a), part III of text.

d. see paragraph (b), part III of text.

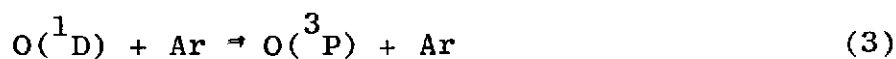
e. see paragraph (c), part III of text.

#### IV. H and O signals from H<sub>2</sub>O photolysis

In these experiments, signal due to H and O was accumulated from the flash photolysis of a mixture of 0.1 torr H<sub>2</sub>O and 100 torr Ar. The ratio of Ar to H<sub>2</sub>O was kept at 10<sup>3</sup> to minimize correction for loss of O(<sup>1</sup>D) via reaction with H<sub>2</sub>O.



This was necessary since the method depends on quantitative conversion of the O(<sup>1</sup>D) initially formed in photolysis to O(<sup>3</sup>P) via deactivation by Ar.



Using the value<sup>31</sup>  $k_7 = 3 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  and, from the results in part V,  $k_3 = 8.3 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , we calculate that the rate of (3) is 2.8 times that of (7). We thus underestimate the O signal by 36%. Higher pressures of argon were avoided since, as calculated from the data given in the appendix, 100 torr of Ar already leads to quenching of the H and O resonance radiation by 42% and 13%, respectively. Thus, lowering the correction for the reaction of O(<sup>1</sup>D) with H<sub>2</sub>O by increasing the Ar pressure to 200 torr would be more than off-set by the extremely large correction due to quenching of the resonance radiation.

Also, a 50% increase in absolute signal was observed in going from 0.1 to 0.3 torr H<sub>2</sub>O, but a proportionately larger correction for O(<sup>1</sup>D) reaction with H<sub>2</sub>O was required. The pressures of H<sub>2</sub>O and Ar employed thus represent a compromise between signal level and the size of corrections made to the observed signal.

Table II presents the data obtained using LiF and sapphire windows on the photo-flash lamp. In Table III we summarize the relative quantum yields for processes yielding H and O in the wavelength interval 105 to 145 nm. This was derived by subtracting the signal obtained with the sapphire window from the signal with the LiF window. Several interesting results may be noted here. First, the total H + O signal from photolysis in the interval 145 to 185 nm (sapphire cut-off to the absorption threshold) is equal to the total signal from photolysis in the interval 105 to 145 nm (LiF minus sapphire) to better than  $\pm 6\%$  (2154 counts and 2393 counts respectively). This indicates that the increased intensity of the flash lamp at longer wavelengths has been essentially compensated for

Table II: H and O signals from H<sub>2</sub>O photolysis<sup>a</sup>

Flash Lamp Filter	Detector	Observed Signal <sup>b</sup>	Corrections to Signal			Corrected Signal
			O( <sup>1</sup> D) Reaction <sup>c</sup>	Ar Quench <sup>c</sup>	Relative Sensitivity <sup>d</sup>	
LiF	H	2784	-	± 0.58	÷ 1.12	4286
	O	150 <sup>e</sup>	÷ 0.64	÷ 0.87	÷ 1.00	269
Sapphire	H	1399	-	± 0.58	÷ 1.12	2154
	O	<10 <sup>e</sup>	÷ 0.64	÷ 0.87	÷ 1.00	<18

a. H<sub>2</sub>O = 0.1 torr, Ar = 100 torr.

b. counts/200 μsec, 100 flashes, 200 joules per flash.

c. see text.

d. see Table I.

e. corrected for O signal observed from 100 torr Ar: 80 counts/200 μsec for LiF filter and 66 counts/200 μsec for sapphire filter

Table III: Relative Quantum Yield for Processes Yielding H and O  
in the Photolysis of H<sub>2</sub>O in the Interval 105 to 145 nm.<sup>a</sup>

Detector	Corrected LiF Signal <sup>b</sup>	Corrected Sapphire Signal <sup>c</sup>	Signal Difference	Relative Yield
H	4286	2154	2132	0.89
O	269	<18	269	0.11

a. H<sub>2</sub>O = 0.1 torr, Ar = 100 torr .

b. counts/200 μsec, 100 flashes, 200 joules per flash, LiF window on the flash lamp (see table II) .

c. same as b except sapphire window on flash lamp (see table II) .

by the decreased absorption coefficients for H<sub>2</sub>O at longer wavelengths. Also, the results in table II show that for the interval 145 to 185 nm (sapphire window), the O signal is less than 1% of the H signal. The uncertainty in the upper limit for this process is as large as the value itself since a small O signal was observed when 100 torr Ar is flowed through the reaction vessel (even after several hours of pumping and heating to remove traces of absorbed water). Finally, we note the relative O yield of 0.11 shown in table III for the interval 105 to 145 nm would only be increased to 0.12 if the corrections for the O signal from 100 torr Ar were neglected.

In order to distinguish between deactivation by Ar of O(<sup>1</sup>D) formed in process C and direct production of O(<sup>3</sup>P) via processes A and F, the experiment using the LiF window was repeated using He instead of Ar. With 100 torr He and 0.1 torr H<sub>2</sub>O and using  $k_7 = 3 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  (ref 31) and  $k_4 < 5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  (see part V), we estimate that the rate of reaction of O(<sup>1</sup>D) with H<sub>2</sub>O (reaction 7) is >>6 times that for reaction with He (reaction 4). Thus

the principal fate of  $O(^1D)$  is reaction with  $H_2O$  and only  $O(^3P)$  formed directly in processes A or F will be detected. The result was that we were unable to detect any O signal when helium was used as the diluent gas. A conservative estimate is that a signal less than 20% of that detected in the presence of Ar could have gone undetected. Hence a upper limit for the combined quantum yield for processes A and F is 0.02.

We therefore conclude, on the basis of the discussion given in part I and that given above, that the O signal measured is due exclusively to process C. Similarly, the H signal must be due solely to processes B and D. If as explained in the introduction we do not distinguish between processes B and D, the H and O signals are then identified with the primary processes:



We distinguish now between results in the two different wavelength intervals. In the first continuum ( $\lambda > 145$  nm, sapphire window) process II accounts for less than 1% of the primary process. This is consistent with results at 185 nm ( $< 1\%$ )<sup>15,32</sup> 174 nm ( $\leq 0.5\%$ )<sup>18</sup> and 147 nm ( $< 1\%$ ,<sup>32</sup> 3%<sup>14,18</sup>

and 2.5%<sup>17</sup>). For photolysis in the second continuum and in the banded region ( $145 > \lambda > 105$  nm), table IV summarizes the comparison between our results and those obtained previously by less direct or less quantitative means. The experiments of McNesby, Tanaka and Okabe<sup>13</sup> are a measure of processes (C) and (E) since the observation depended on measurement of H<sub>2</sub>. In addition, their result (molecular H<sub>2</sub> reduced to 25% when H-atom was scavenged) can be interpreted as a relative quantum yield of 0.25 for process (C) and (E) only under the assumption that atomic hydrogen, initially formed with excess kinetic energy,<sup>15,33</sup> reacts in this system exclusively to abstract H from H<sub>2</sub>O



That is, the implicit assumption is that a 1:1 relationship exists between H formed in the primary process and the scavengable H<sub>2</sub> yield ( $\Phi_{\text{H}} = 0.75$ ). On the other hand, if H is rapidly thermalized and reaction (8) does not occur, then H will disappear by three body recombination



where M can be H<sub>2</sub>O or the wall of the reaction cell. In this case a scavengable yield of H<sub>2</sub> = 75% implies



Table IV:  $\text{H}_2\text{O} + h\nu \rightarrow \text{H}_2 + \text{O}({}^1\text{D})$

Method	Reference	$\lambda$ (nm)	$\Phi$
Product analysis $\text{C}_2\text{D}_4$ Interceptor	McNesby, Tanaka and Okabe <sup>a</sup>	123.6	0.25
"	Alternate assumption (see text)	123.6	0.15
Flash, OH absorption $\text{O}({}^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$	Stuhl and Welge <sup>b</sup> (our estimate)	105 to 185	0.15
Flash, detection of $\text{O}({}^3\text{P})$	this work	105 to 145	0.11

a. reference 13.

b. reference 16.

$$\Phi_H = \frac{2 \times 0.75}{(2 \times 0.75) + 0.25} = 0.85$$

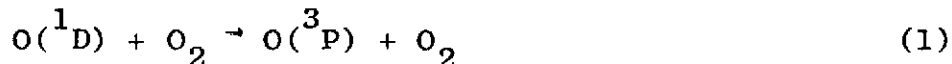
$$\Phi_O = \frac{0.25}{(2 \times 0.75) + 0.25} = 0.15$$

This has been pointed out by Chou, Lo and Rowland<sup>18</sup> for the 147 nm experiments<sup>14</sup> and must be taken into consideration here as well. Nevertheless, the results lead to a relative quantum yield between 0.15 and 0.25 for primary processes leading to O(<sup>1</sup>D) and O(<sup>1</sup>S) depending on the reaction of atomic H occurring. The experiments of Stuhl and Welge<sup>16</sup> do refer only to O(<sup>1</sup>D) formation since O(<sup>1</sup>S) would not have been intercepted by H<sub>2</sub> under the condition of their experiments. Although they used plate photometry for OH absorption and did not attempt to make the experiment quantitative, it can be estimated from their fig 1 that  $\Phi_{II} = 0.15$  for the entire wavelength region 105 to 185 nm. Given their larger uncertainties and their less direct nature, previous experiments are not inconsistent with the present results.

V. Reaction of O(<sup>1</sup>D) with H<sub>2</sub>, Ar and He

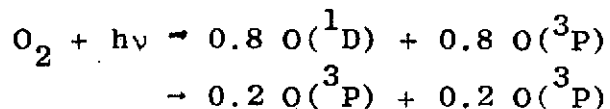
A. O(<sup>1</sup>D) + H<sub>2</sub>

Consider the simple reaction sequence:



The use of a sapphire window on the photoflash lamp in these experiments makes formation of O(<sup>1</sup>S) from O<sub>2</sub> photolysis energetically impossible. The above sequence leads one to expect the O(<sup>3</sup>P) signal to be reduced by one-half upon addition of sufficient H<sub>2</sub> such that all O(<sup>1</sup>D) reacts with H<sub>2</sub>. The results in Table V show that there is excess O(<sup>3</sup>P) formation since the ratio of the signal with H<sub>2</sub>, "S", exceeds one-half the signal in the absence of H<sub>2</sub>, "S<sub>0</sub>", by an average of 20%. Two alternate explanations have been considered:

Case I: Formation of O(<sup>3</sup>P) from O<sub>2</sub> photolysis not accompanied by O(<sup>1</sup>D) (i.e. contribution from a spin forbidden process)



Let S = the H signal at any H<sub>2</sub> pressure and S<sub>∞</sub> = the H signal when the H<sub>2</sub> pressure is large enough to remove all of the O(<sup>1</sup>D) (1 torr or greater). It is readily seen that

Table V: Limiting  $O(^3P)$  signal from Photolysis  
of  $O_2$  upon addition of excess  $H_2$

$H_2$ (torr)	$O(^3P)$ signal <sup>a</sup>		$S/S_0$
	(with $H_2$ ) $S^b$	(no $H_2$ ) $2S_0$	
1 to 21 <sup>c</sup>	885	1540	1.15
1.0 <sup>d</sup>	760	1210	1.25
3.0 <sup>e</sup>	786	1334	1.18

- a. 81 joules per flash, sapphire window on flash lamp.
- b. correction made for quenching of resonance radiation by  $H_2$  (see appendix).
- c. average of six experiments showing no trend ( $\pm 5\%$ ) with  $H_2$  pressure;  $O_2 = 0.5$  torr, He added to total pressure of 50 torr.
- d.  $O_2 = 0.5$  torr, He = 50 torr.
- e.  $O_2 = 1.0$  torr, He = 50 torr.

$$\frac{S}{S_{\infty}} = \frac{k_2 [H_2]}{k_1 [O_2] + k_2 [H_2]}$$

Writing  $S/S_{\infty} \equiv H$  and re-arranging we get

$$\frac{H}{1-H} = \frac{k_2 [H_2]}{k_1 [O_2]}$$

Table VI shows the results of data obtained for  $[O_2] = 1.0$  torr and figure 1 shows the data plotted in this way. A good linear fit to the data is obtained with a least squares slope = 5.09.

Case II: Formation of  $O(^3P)$  via physical deactivation of  $O(^1D)$  by  $H_2$



The limiting value of  $O(^3P)$  signal = 1.2 (table V) requires that  $k_2' = 0.2 k_2$ . Using the same notation as for Case I, we see that

$$\frac{S}{S_{\infty}} = \frac{k_2 [H_2]}{k_1 [O_2] + k_2 [H_2] + k_2' [H_2]} = \frac{k_2 [H_2]}{k_1 [O_2] + 1.2 k_2 [H_2]}$$

Again writing  $S/S_{\infty} \equiv H$  and re-arranging leads to

$$\frac{H}{1-1.2 H} = \frac{k_2 [H_2]}{k_1 [O_2]}$$

Table VI. Flash photolysis of  $O_2$  in the presence of  $H_2$ ; Increase in H signal due to the reaction  $O(^1D) + H_2 \rightarrow H + OH$ .

$H_2^a$	$S^b$	$H = S/S_\infty$	$\frac{H^d}{1-H}$	$\frac{H^e}{1-1.2 H}$
0.0	0	0.00	0.00	0.00
0.1	193	0.40	0.67	0.77
0.2	226	0.47	0.89	1.08
0.5	347	0.72	2.57	5.29
3.0	480 <sup>c</sup>	-	-	-

- a. pressure in torr;  $O_2 = 1.0$  torr, He = 50 torr.
- b. initial counts/100  $\mu$ sec, 30 flashes, 81 joules per flash; sapphire window on flash lamp; signal corrected for quenching by  $H_2$  (see appendix).
- c.  $S_\infty$  is the signal at 3 torr  $H_2$ ; separate experiments showed that this limit was reached by 1.0 torr  $H_2$ .
- d. Case I (see text).
- e. Case II (see text).

An attempt to fit the data in Table VI to this equation was not successful, as shown in figure 2. Instead of being linear, the plot is decidedly curved with the point at  $H_2 = 0.5$  torr a factor of two higher than that estimated by linear extrapolation (dashed line) from the data at lower  $H_2$  pressures.

We therefore conclude that physical deactivation of  $O(^1D)$  by  $H_2$  is not significant and that Case I is applicable here and for the other reaction systems to be discussed below. It should be noted that the result of Paraskevopoulos and Cvetanovic<sup>21</sup> are in agreement with the conclusion that physical deactivation of  $O(^1D)$  by  $H_2$  is negligible compared to chemical reaction.

If we now consider the O signal in this same system and let the O signal in the absence of  $H_2$  be equal to  $2S_o$ , it can be shown that

$$S = 2S_o - 0.8S_o \times \frac{k_2[H_2]}{k_1[O_2] + k_2[H_2]}$$

Writing  $S/S_o = O_x$  and re-arranging leads to

$$\frac{2 - O_x}{O_x - 1.2} = \frac{k_2[H_2]}{k_1[O_2]}$$

Data obtained at  $[O_2] = 1.0$  torr are given in Table VII and plotted in this way in figure 3. A good linear fit to the

Table VIII. Effect of  $H_2$  on the  $O(^3P)$  Signal  
in the Flash Photolysis of  $O_2$

$H_2$ (torr)	$S^a$	$O_x \equiv S/S_o$	$\frac{2-O_x}{O_x-1.2}$
0.0	906 <sup>b</sup>	2.00	0.00
0.1	797 <sup>c</sup>	1.76	0.28
0.1	1276 <sup>d</sup>	1.91	
0.2	1134 <sup>d</sup>	1.70	0.60
0.4	715 <sup>c</sup>	1.58	1.11
0.5	1002 <sup>d</sup>	1.50	1.67
0.7	647 <sup>c</sup>	1.43	2.49
0.0	1334 <sup>b</sup>	2.00	0.00

a. initial counts/200 $\mu$ sec, 81 joules per flash, sapphire window on flash lamp;  $O_2 = 1.0$  torr, He = 50 torr.

b.  $2 S_o$  is the signal in the absence of  $H_2$ .

c.  $S_o = 453$ ; 4 flashes, average of two experiments.

d.  $S_o = 667$ ; 10 flashes, single experiment.



data is obtained with a least squares slope = 3.37. Combining this with the value determined above from the H signal (Case I) leads to the average value

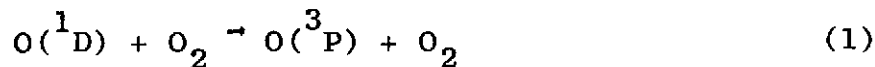
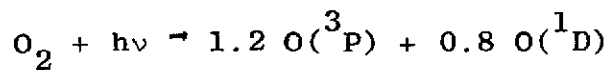
$$\frac{k_2}{k_1} = 4.23 \pm 0.86$$

Taking  $k_1 = (6 \pm 1) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  (ref 19), we obtain the result

$$k_2 = (2.5 \pm 1.0) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

B. O(<sup>1</sup>D) + Ar

In light of the previous discussion, the following mechanism may be considered.



Thus addition of Ar to a fixed O<sub>2</sub> + H<sub>2</sub> mixture should lead to an increase in the O(<sup>3</sup>P) signal. Using the same notation as before, we have

$$O_x \equiv \frac{S}{S_o} = 1.2 + 0.8 \times \frac{k_1[\text{O}_2] + k_3[\text{Ar}]}{k_1[\text{O}_2] + k_2[\text{H}_2] + k_3[\text{Ar}]}$$

This can be re-arranged to the more convenient form

$$\frac{4.23 (O_x - 1.2)}{2 - O_x} = 0.5 + \frac{k_3}{k_1} (\text{Ar})$$

where we have substituted  $k_2/k_1 = 4.23$  from the previous section,  $H_2 = 1.0$  torr, and  $O_2 = 0.5$  torr. Two sets of data obtained at various Ar pressures are shown in Table VIII and plotted according to this equation in figures 4 and 5. From the least squares fit to these independent sets of data we obtain

$$\text{slope} \equiv \frac{k_3}{k_1} = (1.38 \pm 0.16) \times 10^{-2}$$

Taking as before  $k_1 = (6 \pm 1) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$

(ref 19), we obtain the result

$$k_3 = (8.3 \pm 2.3) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

### C. $O(^1D) + \text{He}$

The equations employed are exactly the same as for Ar deactivation. Deactivation of  $O(^1D)$  by He would lead to an increase in the  $O(^3P)$  signal with increasing He. The data in Table IX in fact, show that the average signal appears to decrease slightly although the difference between the signals is probably not significant. To put

Table VIII. Effect of Ar on the  $O(^3P)$  Signal  
in the Flash Photolysis of  $O_2$   
in the Presence of  $H_2$

Ar (torr)	$H_2$ (torr)	$S^a$	$O_x \equiv S/S_o$	$\frac{4.23(O_x - 1.2)}{2 - O_x}$
50	0.0	2004 <sup>b</sup>	-	-
50	1.0	1324 <sup>c</sup>	1.32	0.75
100	1.0	1433 <sup>c</sup>	1.43	1.71
150	1.0	1496 <sup>c</sup>	1.49	2.41
50	0.0	1994 <sup>b</sup>	-	-
50	1.0	1348 <sup>d</sup>	1.35	0.97
100	1.0	1465 <sup>d</sup>	1.47	2.15
150	1.0	1518 <sup>d</sup>	1.52	2.83

a. initial counts/200 $\mu$ sec, 81 joules per flash, 15 flashes,  
sapphire window on flash lamp;  $O_2$  - 0.5 torr; signal  
corrected for quenching by Ar (see appendix)

b.  $2 S_o$  is the signal in the absence of  $H_2$ .

c.  $S_o = 1002$ .

d.  $S_o = 997$ .

Table IX. Effect of He on O(<sup>3</sup>P) Signal in the Flash Photolysis of O<sub>2</sub> in the Presence of H<sub>2</sub><sup>a</sup>

He (torr)	O( <sup>3</sup> P) Signal		Average Signal S
	Observed <sup>b</sup>	Corrected <sup>c</sup>	
50	780	804	
50	772	796	801
50	780	804	
400	559	736	
400	612	805	771
400	586	771	

a. O<sub>2</sub> = 0.5 torr, H<sub>2</sub> = 1.0 torr

b. counts/200μsec, 5 flashes, 70 joules per flash;  
sapphire window on the flash lamp

c. corrected for quenching of resonance radiation by He;  
see the appendix.

an upper limit on  $k_4$ , we may take the maximum value for the  $O(^3P)$  signal observed using 400 torr He, i.e.  $S = 805$ .

Since  $S_o = 605$ ,  $O_x \equiv S/S_o = 1.33$ . We then calculate the left hand side of the equation

$$\frac{4.23 (O_x - 1.2)}{2 - O_x} = 0.5 + \frac{k_4}{k_1} (\text{He})$$

to be equal to 0.8. Substituting this, we obtain the result for He = 400 torr

$$\frac{k_4}{k_1} < \frac{0.3}{400}$$

With  $k_1 = 6 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  (ref.19), we then obtain the rather extreme upper limit for  $k_4$

$$k_4 < 5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.$$

#### D. Comparison with Previous Determinations

Table X summarizes the comparison of our results with some of the more recent results obtained, both absolute and relative. The relative measurements have been obtained using direct spectroscopic methods, such as those employed in this study, and indirect methods such as final product analysis. A detailed comparison with all available data has not been attempted here. As mentioned in the introduction

Table X. Comparison of Rate Constants  
for O(<sup>1</sup>D) Reactions

Reaction	k(cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	absolute or relative	direct or indirect	reference
O( <sup>1</sup> D) + H <sub>2</sub>	1.7 x 10 <sup>-10</sup>	relative <sup>a</sup>	direct	20
	4.2 x 10 <sup>-10</sup>	relative <sup>b</sup>	indirect	21
	6.7 x 10 <sup>-10</sup>	relative <sup>b</sup>	direct	22
	2.7 x 10 <sup>-10</sup>	absolute	direct	23
	2.5 x 10 <sup>-10</sup>	relative <sup>a</sup>	direct	this work
O( <sup>1</sup> D) + Ar	2 x 10 <sup>-12</sup>	relative <sup>b</sup>	indirect	24
	2 x 10 <sup>-12</sup>	relative <sup>b</sup>	indirect	25
	7.1 x 10 <sup>-13</sup>	absolute	direct	26
	8.3 x 10 <sup>-13</sup>	relative <sup>a</sup>	direct	this work
O( <sup>1</sup> D) + He	< 10 <sup>-12c</sup>	relative <sup>b</sup>	indirect	21
	5.4 x 10 <sup>-12</sup>	relative <sup>a</sup>	indirect	27
	< 7 x 10 <sup>-16</sup>	absolute	direct	26
	< 5 x 10 <sup>-14</sup>	relative <sup>a</sup>	direct	this work

a. relative to O<sub>2</sub>, k = 6 x 10<sup>-11</sup> cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> (ref. 19).

b. relative to CO<sub>2</sub>, k = 2.1 x 10<sup>-10</sup> cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> (ref. 31).

c. our estimate of upper limit.

we have directed our attention to information required for the  $\text{H}_2\text{O}$  photolysis experiment. In the case of  $\text{O}(^1\text{D}) + \text{H}_2$  we were particularly concerned with distinguishing between chemical reaction and physical deactivation. It appears that the only previous study<sup>21</sup> to examine this carefully is also the most indirect while the only direct and absolute measurement<sup>23</sup> does not distinguish between chemical reaction and physical deactivation. Our finding that physical deactivation is negligible is consistent with the product analysis results.<sup>21</sup> In addition, our result  $k_2 = (2.5 \pm 1.0) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  is in excellent agreement with the absolute value  $k_2 = (2.7 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  reported by Heidner and Husain.<sup>23</sup> It should be noted that our rate constants are all measured relative to that for the reaction  $\text{O}(^1\text{D}) + \text{O}_2$  which has been the subject of four absolute, direct studies in three different laboratories.<sup>19</sup>

In the case of quenching by Ar and He, we were more concerned with large discrepancies in the literature for the values of  $k_3$  and  $k_4$  respectively. Thus the recent absolute value for  $k_3$ <sup>26</sup> is nearly three times smaller than two previous determinations<sup>24,25</sup> using product analysis. Our result of

$k_3 = 8.3 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  supports the

lower value obtained by Heidner and Husain.<sup>26</sup> Finally we

note that our work as well as most of the recent experiments

have failed to detect any quenching by He and thus only

an upper limit can be placed on the value for  $k_4$ .

### Appendix

Corrections for quenching of H and O resonance radiation by H<sub>2</sub>, He and Ar have been made in these experiments. The data for H was obtained from flash photolysis of 0.2 torr CH<sub>4</sub> while the data for O was obtained from flash photolysis of 0.5 torr O<sub>2</sub>. In all cases, the signal decreased linearly with pressure of the quenching gas. The data are collected in Table XI and for convenience in these experiments quenching is given as percent reduction in resonance signal per torr of quenching gas. It should be noted that these results for quenching of H resonance radiation by H<sub>2</sub> and He are in reasonable agreement with those reported by Braun et al.<sup>34</sup>

Table XI: Quenching of H and O Resonance Radiation by H<sub>2</sub>, He and Ar.

Radiation	Percent per torr		
	H <sub>2</sub> <sup>a</sup>	He <sup>b</sup>	Ar <sup>c</sup>
H	2.9%	0.13%	0.42%
O	< 0.25%	0.06%	0.13%

a. Pressure range 7 to 21 torr; b. 50 to 400 torr;

c. 50 to 200 torr.



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## FIGURE CAPTIONS

Fig. 1. Effect of  $H_2$  pressure on H signal in the photolysis of 1 torr  $O_2/50$  torr He,  $H = S/S_\infty$ . (Case I - see text).

Fig. 2. Effect of  $H_2$  pressure on H signal in the photolysis of 1 torr  $O_2/50$  torr He,  $H = S/S_\infty$ . (Case II - see text).

Fig. 3. Effect of  $H_2$  pressure on the  $O(^3P)$  signal in the photolysis of 1 torr  $O_2/50$  torr He.  $O_x = S/S_o$ .

Fig. 4 and Fig. 5 Effect of Ar pressure on the  $O(^3P)$  signal in the photolysis of 0.5 torr  $O_2/1$  torr  $H_2/50$  torr He;  $O_x = S/S_o$ .

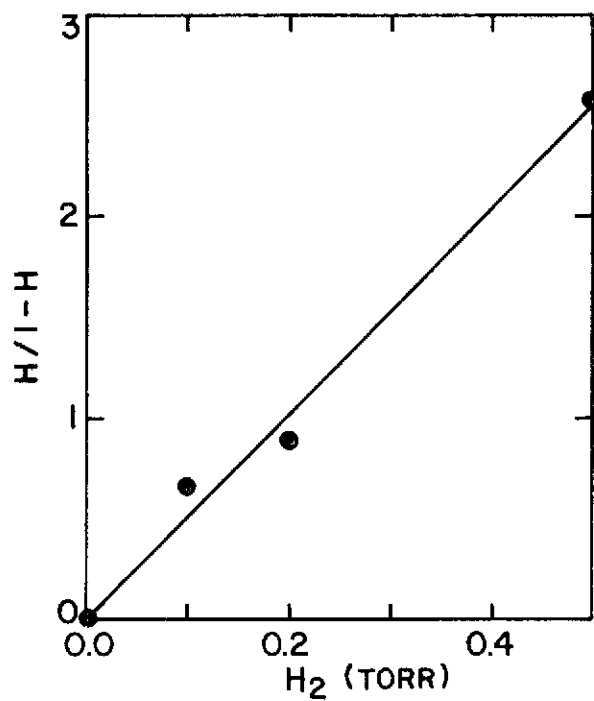


FIGURE 1

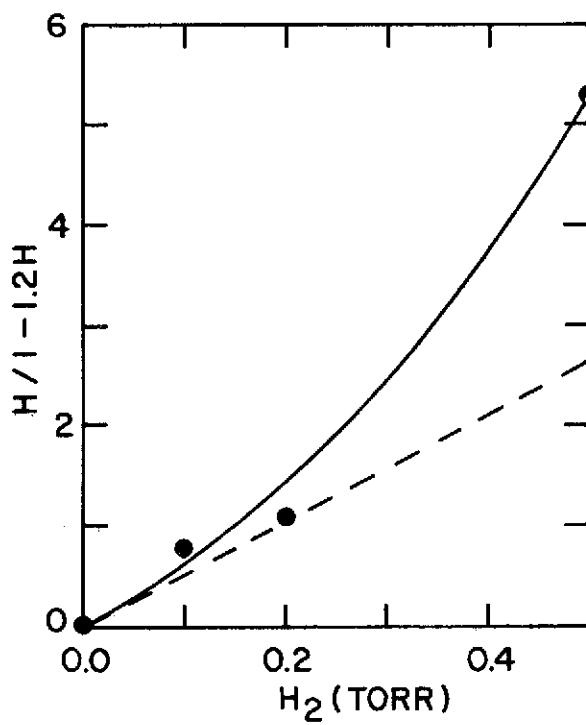


FIGURE 2

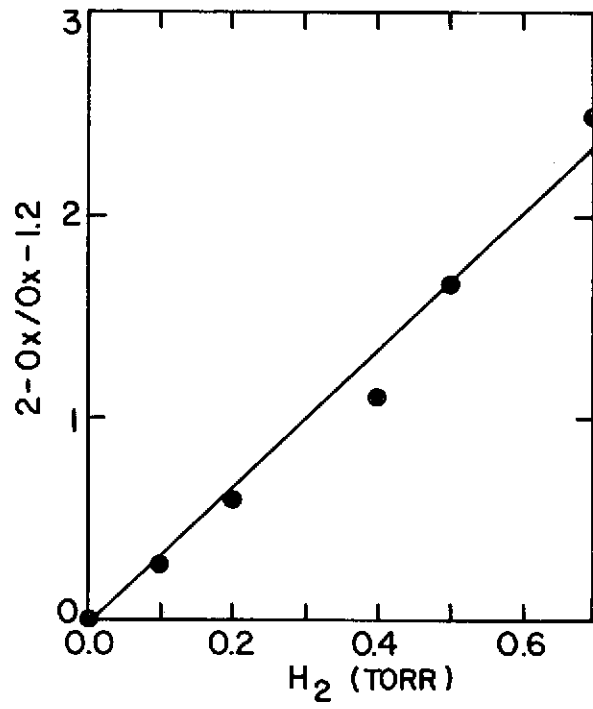


FIGURE 3

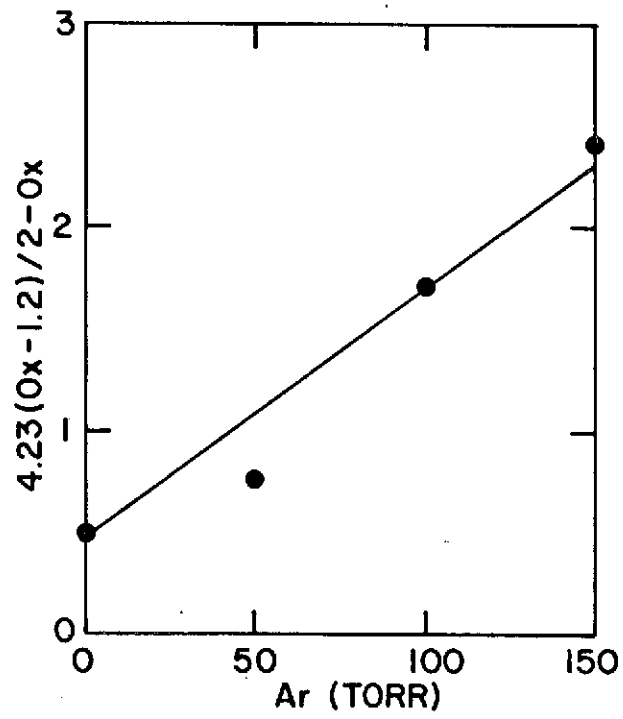


FIGURE 4

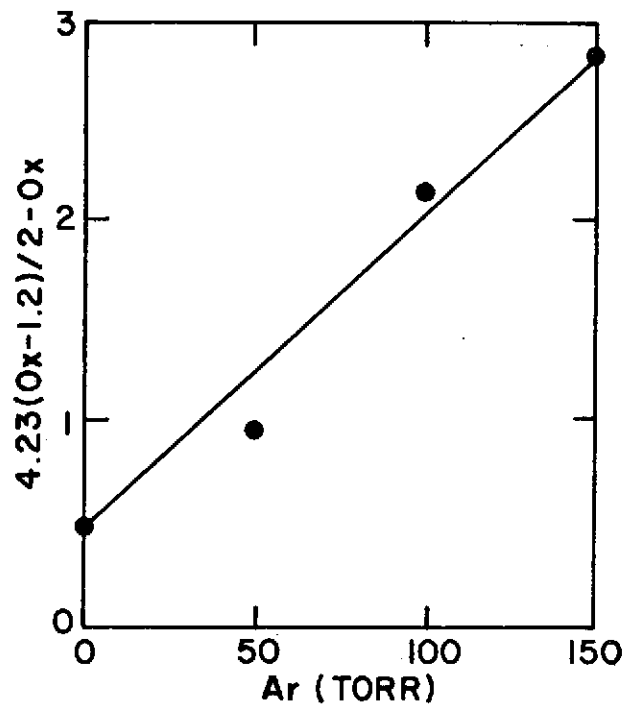


FIGURE 5