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O (^{1}D) Production in Ozone Photolysis Near 310 nm

C. -L. Lin

W. B. DeMore

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Relative quantum yields of O(^{1}D) production, ϕ, in ozone photolysis from 275nm to 334nm have been determined in the gas phase at 233K. The O(^{1}D) was monitored by means of its reaction with isobutane to form isobutyl alcohol. The light source was a high pressure mercury lamp combined with a monochromator, with a bandwidth of 1.6nm. The results show a constant ϕ below 300nm, which is taken as unity on the basis of previous work. There is a very sharp fall-off in ϕ which is centered at 308nm. At 313nm ϕ is not greater than 0.1.

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PREFACE

The work described in this report was performed by the Space Sciences Division of the Jet Propulsion Laboratory.

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FIGURE

ABSTRACT

Relative quantum yields of O(^{1}D) production, ϕ, in ozone photolysis from 275nm to 334nm have been determined in the gas phase at 233K. The O(^{1}D) was monitored by means of its reaction with isobutane to form isobutyl alcohol. The light source was a high pressure mercury lamp combined with a monochromator, with a bandwidth of 1.6nm. The results show a constant ϕ below 300nm, which is taken as unity on the basis of previous work. There is a very sharp fall-off in ϕ which is centered at 308nm. At 313nm ϕ is not greater than 0.1.

INTRODUCTION

Singlet atomic oxygen, $O(^1D)$, plays an important role in stratospheric chemistry, and its rates of production and destruction must be known reliably. The most important source of $O(^1D)$ in the stratosphere is ozone photolysis at wavelengths near 300nm. The importance of this wavelength region results from overlap of decreasing ozone absorption and increasing solar radiance as wavelengths increase above 300nm. Unfortunately, the mechanism of ozone photolysis changes near 310nm, and previous work[1,2,3] has indicated a sharp decline in $O(^1D)$ yields. Several problems remain in the interpretation of the early data. For example, the experiments of DeMore and Raper[1,2] were done in low temperature solvents, so that the results may not be directly applicable to stratospheric conditions. Further, the work of Castellano and Schumacher[4] seems to indicate a unit $O(^1D)$ quantum yield at 313nm, in conflict with the early work. A very recent paper[5] reports a quantum yield of 0.5 ± .03 at 313nm, a value which is still much higher than previously accepted by most aeronomists.[6]

In the present work we have measured the relative $O(^1D)$ quantum yields in the wavelength range 275nm to 334nm. Our results show fall-off of ϕ beginning at 305nm, reaching zero at 320nm. At 313nm ϕ is 0.08 or less, in good agreement with the previous work of Jones and Wayne.[3]

EXPERIMENTAL

The $O(^1D)$ was detected by its reaction with isobutane to form isobutyl alcohol. This is the only reaction which gives this product under the experimental conditions.

$$O(^1D) + iso\text{-}C_4H_{10} \longrightarrow CH_3CH(CH_3)CH_2OH \qquad (1)$$

Not all $O(^1D)$ produced leads to isobutyl alcohol. In the usual reaction mixture ($13.33 KN/m^2$ isobutane, $13.33 KN/m^2$ O_2, $2.4 KN/m^2$ O_3, and $275.8 KN/m^2$ SF_6), some $O(^1D)$ is quenched by O_2, and only a part of the $O(^1D)$ which reacts with isobutane gives isobutyl alcohol, because abstraction of hydrogen occurs to some extent even at high pressures.[7] Also, some $O(^1D)$ attacks the tertiary hydrogen and gives t-butyl alcohol. Nevertheless, for a constant mixture composition, the yield of isobutyl alcohol is proportional to the $O(^1D)$ produced, which is the necessary condition for the present experiment. The oxygen protects ozone from destruction by radical attack.

Isobutyl alcohol is not formed by $O(^3P)$, which attacks only the tertiary hydrogen. Under the reaction conditions, this process leads to a substantial yield of t-butyl alcohol. The mechanism is, of course, more complex than the simple insertion reaction which is characteristic of $O(^1D)$. In principle, the t-butyl alcohol yield can be used to monitor the $O(^3P)$ yield, in the same way that isobutyl alcohol is used to monitor the $O(^1D)$ yield. Unfortunately, there is a dark reaction between ozone and isobutane which forms t-butyl (but no isobutyl) alcohol. Although this dark reaction is fairly slow at the experimental temperature (233 K) some experiments at long wavelengths required very long radiation times ($\sim 8.64 \times 10^4$ sec) and the amount of t-butyl alcohol formed by the dark reaction was not negligible compared to the photochemical yield, and could not be corrected for in a quantitative manner. Nevertheless, the yields of t-butyl alcohol did show qualitatively that decline of the $O(^1D)$ yield was accompanied by an increase in the O(^{3}P) yield, in agreement with earlier work in liquid nitrogen.[2]

The photolyses were carried out in a 5-cm vacuum-jacketed brass cylindrical cell (4.1 cm I.D) with quartz windows sealed at both ends. The cell was cooled by liquid CO_2 (in a separate chamber) held at about 790.8KN/m^2 by means of a pressure regulator. Oxygen (Matheson ultra-high purity grade) was used directly from the tank. Ozone was prepared by a Tesla coil discharge in O_2 and was stored at 77K. Research Grade isobutane (Matheson) was further purified by freeze and thaw pumping. The SF_6 was passed over Ascarite to remove CO_2.

The ozone optical densities were measured with a Cary Model 11 spectrophotometer.

The light source was a B-H6 mercury lamp (General Electric) in combination with a Bausch and Lomb monochromator (Cat. No. 33-86-45, dispersion 1.6nm, f/4.4). A slit width of 1.0 mm was used at both entrance and exit slits. As a test of monochromaticity, the emerging light was examined with a second monochromator of the same type, using 0.1 mm slits and a photometric detector. At three wavelengths in the region of interest (310nm, 313nm, and 318nm) the bandwidths were verified to be 1.6 ± 0.2nm, with negligible scattered light throughout the range 200-350nm The wavelength scale was calibrated with a low pressure mercury lamp. Light intensities emerging from the monochromator were measured with an Epply thermopile. The percent decomposition of O_3 was less than 3%.

After photolysis, which varied from about 7.2×10^3 to 8.64×10^4 sec depending on wavelength, the products were separated from the reaction mixture by pumping through a trap at 178K. The yields of iso- and t-butyl alcohol were measured by means of a 4-ft Porapak Q gas chromatographic column at 423K.

RESULTS

Quantum yields of $O(^1D)$ production in the primary step of ozone photolysis are plotted as a function of wavelength from 275nm to 334nm in Fig. 1. For comparison, data from references 1-5 are included. The quantum yields were normalized relative to the mean value from 275nm to 300nm, because previous measurements[2] have shown that ϕ is unity in that range. As expected, ϕ is fairly constant in the range 275nm to 305nm At around 305nm, ϕ drops sharply and approaches zero at about 320nm These results, of course, reflect not only the true λ dependence of ϕ, but also the fact that the light is not strictly monochromatic. (See Discussion Section.) The data point at 275nm in Fig. 1 was taken with an ozone pressure of $0.267 KN/m^2$ rather than the usual $2.4 KN/m^2$ as a test for dependence on ozone concentration. The resulting data point for ϕ showed no difference from the other points, indicating that reactions of $O(^1D)$ or other species with ozone do not significantly affect the isobutyl alcohol yield.

DISCUSSION

From energetic considerations, the wavelength limit for the process

$$O_3 \longrightarrow O_2(^1\Delta) + O(^1D) \qquad (2)$$

is 310nm, based on 189.95KJ/mol and 94.14KJ/mol for the electronic excitation energies of $O(^1D)$ and $O_2(^1\Delta)$, respectively, and 101.67KJ/mol for the bond dissociation energy of O_3 at 0 K. The latter quantity is uncertain by at least 1.67KJ/mol, which corresponds to about 1.3nm in the wavelength range near 310nm.

Our data in Fig. 1 indicate a sharp break in ϕ at 308nm, which agrees well with the predicted wavelength limit for process 2, within the experimental uncertainty of the O_3 bond energy. Lack of sharpness in the fall-off of ϕ can be ascribed almost entirely to the finite bandwidth of the light source, which was about 1.6nm (half-bandwidth). Thus, for calculation of $O(^1D)$ production rates in O_3 photolysis, ϕ can be considered to be unity below 308nm and zero at longer wavelengths.

Previous measurements of the wavelength dependence of ϕ in liquid N_2 solution[1] showed a break beginning at about 300nm. Since those experiments utilized the same light source as the present work, the difference is evidently real and is probably due to solvent effects, as discussed in the earlier paper.

The present results agree well with the data of Jones and Wayne,[3] but not with those of references 4 and 5. The reasons for the discrepancies are not known.

This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration.

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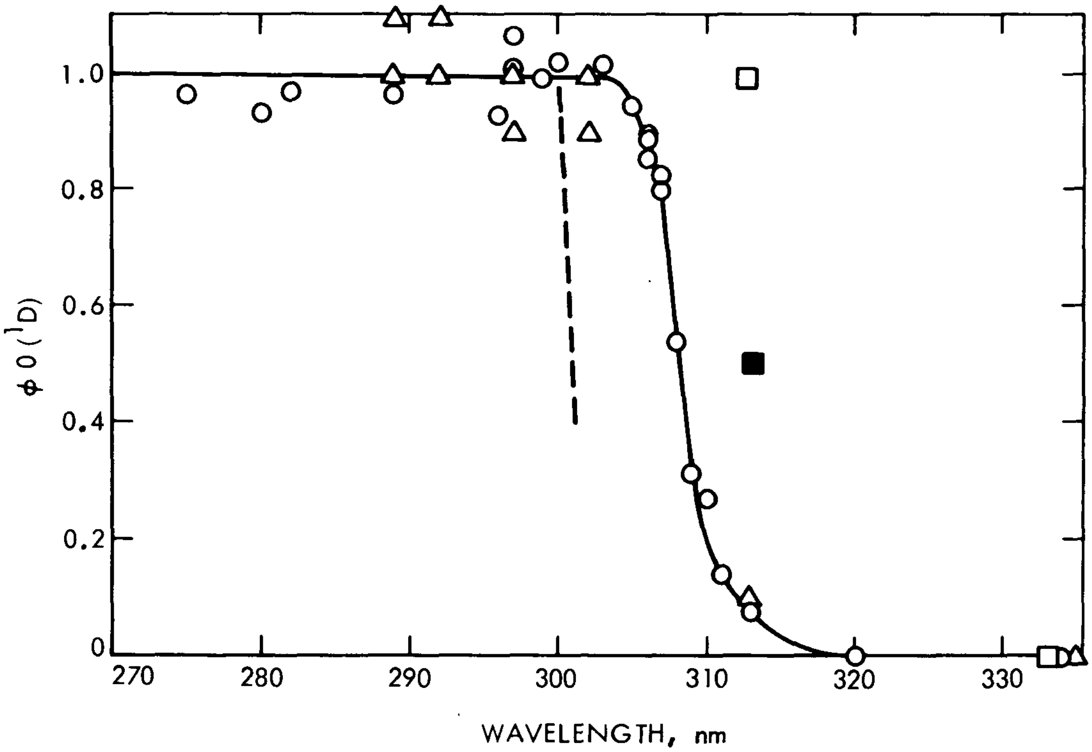

Fig. 1. The O(^{1}D) quantum yield as a function of wavelength. O and —, this work; △, Jones and Wayne (reference 3); □, Castellano and Schumacher (reference 4); ■, Simonaitis *et al.* (reference 5); ---, DeMore and Raper (77 K in liquid N_2, reference 1).