

# Absolute Rate Constants for the Reaction of Atomic Oxygen with Ethylene over the Temperature Range 232–500°K

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(Received 20 September 1971)

Rate constants for the reaction of atomic oxygen with ethylene were measured over a temperature range of 232–500°K using the flash photolysis–resonance fluorescence technique. The rate constant at room temperature was also determined using a flash photolysis–kinetic absorption spectroscopy system and a discharge-flow system coupled to a mass spectrometer. Within the experimental errors of the three techniques, good agreement was found for the rate constant at 298°K. The bimolecular rate constant was also found invariant to changes in both total pressure and reactant concentration. Over the temperature range of the experiments, the rate data could be fitted by a simple Arrhenius expression of the form,

$$k = 5.42 \pm 0.30 \times 10^{-12} \exp[(-1130 \pm 32 \text{ cal mole}^{-1}) / RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}.$$

## INTRODUCTION

The rate of the reaction of atomic oxygen  $O(^3P)$  with ethylene has been extensively studied.<sup>1–13</sup> There are, however, significant discrepancies in the literature, both in the absolute value of the rate constant at room temperature and in the reaction's temperature dependence. Room temperature rate constants, for example, have been reported which range from  $3.6 \times 10^{-13}$  s<sup>8</sup> –  $9.5 \times 10^{-13}$  cm<sup>3</sup> molecules<sup>-1</sup>·sec<sup>-1</sup>.<sup>11</sup> The activation energy for the reaction was reported by Elias<sup>11</sup> to be 1.6 kcal mole<sup>-1</sup>, while Westenberg and deHaas<sup>10</sup> found an apparent activation energy that increased with temperature from 1.1 to 2.8 kcal mole<sup>-1</sup>. Furthermore, the relative rate data of Cvetanović<sup>1</sup> imply an activation energy for the ethylene reaction of 2.6 kcal mole<sup>-1</sup>, assuming zero activation energy for the reaction of atomic oxygen with tetramethylethylene. Since this reaction is of great importance both as the prototype atomic oxygen–alkene reaction and as a primary standard against which the rates of other atomic-oxygen reactions may be measured, we have re-examined the kinetics of this reaction using three different experimental techniques in three different laboratories. The principle objective was the determination of the rate coefficient under conditions free from complicating secondary reactions, thereby resolving the earlier discrepancies.

## EXPERIMENTAL

The three experimental techniques used in this work were: (1) a discharge-flow system with mass spectrometric detection (located in the Elementary Processes Section of the National Bureau of Standards); (2) a flash photolysis–resonance fluorescence apparatus (lo-

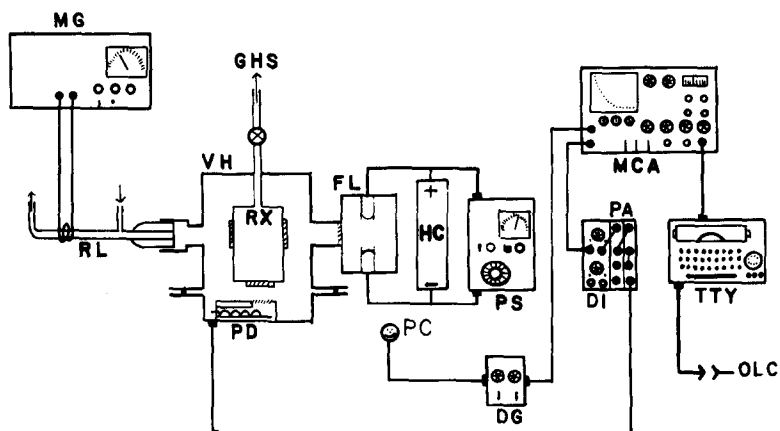
cated at the University of Maryland); and (3) a flash photolysis–kinetic absorption system (located in the Photochemistry Section of the National Bureau of Standards). All three techniques were used to measure the rate constant of the atomic oxygen–ethylene reaction at room temperature; the temperature dependence of the reaction was then established using the resonance fluorescence apparatus.

### Flash Photolysis Resonance Fluorescence

The application of flash photolysis–resonance fluorescence to kinetic studies has been discussed previously.<sup>14–17</sup> The apparatus, shown schematically in Fig. 1, consists of a thermostated reaction cell centered in a vacuum housing; a spark-discharge flash lamp perpendicular to one face of the cell (the point of discharge was 18 cm from the center of the cell); an atomic-oxygen resonance lamp perpendicular to another face (the discharge zone was 19 cm from the center of the cell); and a photodetector (a magnetic electron multiplier using either a copper iodide or tungsten photocathode) perpendicular to the base of the cell at a distance of 9 cm. All windows (2.5-cm diam) were lithium fluoride, except for a calcium fluoride window between the resonance lamp and reaction cell which effectively blocked all Lyman  $\alpha$  radiation (1216 Å) emitted by the resonance lamp. Honeycomb collimation above the detector and collimating rings between the resonance lamp and reaction cell were used to reduce the scattered light signal.

The atomic-oxygen resonance lamp was of the same construction as that described by Davis and Braun.<sup>18</sup> Ultrahigh-purity helium was pumped through a multi-coiled liquid-nitrogen cold trap and then through the

FIG. 1. Schematic drawing of the flash photolysis-resonance fluorescence apparatus. RL, resonance lamp; MG, microwave generators; PS, power supply; FL, flash lamp; RXC, reaction cell; VH, vacuum housing; PD, photon detector; PC, photocell; DG, delay generator; PA, pulse amplifier; DI, voltage discriminator; MCA, multichannel analyzer; TTY, teletype; and OLC, on-line 1108 Univac computer for data processing.



lamp at a pressure of about 1 torr (1 torr = 133 N m<sup>-2</sup>). A microwave discharge through the ultrahigh-purity helium (which still contained trace quantities of oxygen) produced the oxygen resonance triplet at 1303.5 Å which, when examined on a vacuum monochromator, showed significant line reversal in the multiplet ( $J=2$ ).

The photolysis flash was produced by a spark discharge through nitrogen. With about 30 torr of nitrogen flowing through the flash lamp, a 10- $\mu$ f rapid discharge capacitor was charged to the breakdown potential of the gas. The voltage at which the discharge took place, and therefore the flash intensity, could be controlled by adjusting the pressure of the gas in the lamp. Using ethylene actinometry (taking  $\Phi_{C_2H_2} = 1$ )<sup>19</sup> the photon flux reaching the reaction cell for a flash intensity of 45 J was determined to be about  $4 \times 10^{12}$  photons cm<sup>-2</sup>.

The temperature of the reaction cell could be controlled from about 220 to 500°K by either passing cold nitrogen gas through tubes in the reaction cell block or by passing current through resistance wire wound through the reaction cell block. The temperature was determined with a Chromel-Alumel thermocouple embedded in the reaction cell.

Processing of the electrical signal from the photodetector was as follows: Voltage pulses from the detector were amplified by three wide-band amplifiers (over-all gain of 1000); passed through a voltage discriminator to remove low level noise; and finally, recorded on multichannel analyzer operated in the multi-scaling mode.

In a typical experiment, the reaction cell was filled with a mixture of several millitorr of ethylene, about 1 torr of oxygen, and several torr of helium as a diluent gas. This mixture was then flash photolyzed, producing from  $10^{11}$ – $10^{13}$  oxygen atoms per cubic centimeter, depending on the amount of molecular oxygen present and the flash intensity. The oxygen atoms produced by the flash lamp absorbed a small amount of the atomic-oxygen resonance radiation from the resonance lamp (operated cw) and subsequently fluoresced with a lifetime of  $10^{-8}$ – $10^{-9}$  sec. A small fraction of this fluores-

cence was monitored by the photodetector and the resulting signal recorded as a function of time on the multichannel analyzer. Since pulse counting techniques were employed, statistical fluctuations in the signal were reduced by adding the results of many flashes to produce one kinetic curve. As necessary, the gas mixture was changed during the experiment to ensure that the total consumption of ethylene never exceeded about 3%.

Under our conditions of low atom concentration and short sampling path length, the percent absorption of the resonance radiation was low and therefore directly proportional to the atom concentration. This was tested experimentally by varying the atom concentration (i.e., flash intensity) and observing that the fluorescence signals were directly proportional to the flash intensity. Since the fluorescence was proportional to the absorption, it too was proportional to the atom concentration. Even at the highest atom concentrations, the optically thick resonance lamp ensured linearity. The decay in fluorescence signal was used directly to follow the decay in atom concentration in the reaction zone.

The experiments were performed under first-order conditions with ethylene in large excess over atomic oxygen. The first-order rate constant was then used to derive the second-order rate constant for the reaction.

The basic rate expression for the loss of atomic oxygen in this system is

$$-d[O]/dt = k[O][C_2H_4] + k'[O],$$

where  $k$  is the bimolecular rate constant for the reaction and  $k'$  represents the loss of atomic oxygen due to diffusion from the reaction zone and from reaction of O with molecular oxygen. This expression can be integrated to give

$$\ln[O]_0/[O] = (k[C_2H_4] + k')t = k_{\text{exp}}t.$$

The value of  $k'$  was determined from the O-atom decay in the absence of ethylene. The correction in  $k_{\text{exp}}$  due

to  $k'$  generally ranged from 5% to 15% (being as much as 30% in only a few instances). An alternative method of solution involves plotting  $k \exp$  vs  $[C_2H_4]$  and calculating  $k$  from the slope. Using this procedure, no correction need to be made.

With pulse counting techniques, the statistical uncertainty in a measurement can be estimated as the square root of the number of counts. In these experiments, there is a "background" associated with scattered light from the resonance lamp, and the error in determining this quantity must be similarly considered. Typically, statistical fluctuations in experiments where  $\sim 1000$  counts had been accumulated per channel resulted in random errors in the rate constants on the order of 5%. This number was checked by making multiple runs on a single mixture and comparing the standard deviation of these several runs, with the uncertainty calculated from a single run. Good agreement was found between these two approaches. The over-all precision of the experimental technique was further increased by adding the results from several runs such that under one set of experimental conditions the uncertainty approached 3%. This limiting uncertainty reflects the precision with which the various gas mixtures could be made up.

#### Flash Photolysis-Kinetic Absorption Spectroscopy

The use of the flash photolysis-kinetic absorption spectroscopy technique in the study of atom-molecule reactions has also been discussed previously.<sup>16</sup> The apparatus used was similar to that described above for flash photolysis-resonance fluorescence except that the vacuum housing was attached to the entrance slit of a  $\frac{1}{2}$ -m vacuum ultraviolet monochromator in line with the resonance lamp. For these experiments, the resonance lamp was made optically thin by making the discharge zone physically thin and in close proximity to the lamp window. As before, a photodetector was placed perpendicular to both the resonance lamp and the flash lamp. A second photodetector was positioned beyond the exit slit of the monochromator and connected to a multichannel analyzer. This arrangement allowed both absorption and fluorescence measurements to be made on the oxygen resonance line as a function of time. The resolution of the monochromator was sufficient to allow all three  $J$  levels of the oxygen line to be observed independently. Unlike the kinetic measurements using resonance fluorescence, kinetic absorption spectroscopy requires that a sufficient atom concentration be produced to give an initial absorption of the resonance radiation of greater than 10%. (It was for this reason that the thin lamp described above was used.) Under these conditions, the absorption is not strictly a linear function of the atom concentration. As before,<sup>16</sup> this nonlinearity was corrected for using calculated growth curves.<sup>20</sup> The correction was always less than 15% of the calculated rate constant.

As in the case of the fluorescence measurements, the ethylene concentration was in large excess over that of atomic oxygen, and the same kinetic expressions hold. The general experimental procedure, therefore, was the same as that used in the resonance fluorescence technique. The apparatus used for kinetic absorption measurements was also used for making resonance fluorescence measurements at NBS at known atom concentrations. In these studies both a tungsten and a copper iodide photocathode were used. The atom concentrations in these fluorescence experiments were determined from ratios of the flash intensities, previously calibrated in the kinetic absorption measurements.

#### Flow Discharge-Mass Spectrometer

Since most of the previously measured absolute rate constants for reaction of atomic oxygen with ethylene involved flow systems, two of which used mass spectrometric detection, we have also employed a flow system coupled to a mass spectrometer to measure the rate of this reaction. The apparatus, which has been described elsewhere,<sup>21</sup> consists of a 20-mm-i.d. borosilicate glass reactor with a central moveable inlet. Atomic oxygen was produced by means of a microwave discharge in a mixture of a few percent oxygen in argon. Ethylene was added downstream through a moveable inlet, which defined the start of the reaction zone. The end of the reaction zone was defined by a pinhole leak situated directly above the ionizing electron beam of the mass spectrometer. In this system, kinetic runs were performed with an excess of atomic oxygen; hence first order kinetics were observed for the loss of ethylene. Rate constants were then determined by measuring the ratio of the ethylene partial pressure at the mass spectrometer leak with the discharge off and on. As discussed previously,<sup>21</sup> the rate constant is given by

$$k = \ln(R_o/R)/[O]_{av.}$$

Typically, the partial pressure ratio and the atomic-oxygen concentration were determined at different reaction times and the resulting rate constants averaged. Conditions were such that stoichiometric corrections were not required. The method of determining these conditions has been discussed previously.<sup>21</sup>

The ethylene used in all three laboratories consisted of research-grade ethylene (stated purity 99.9%) and was used after two to three outgassings at liquid-nitrogen temperature. Other reagents (helium and oxygen) were likewise the same in all three labs and consisted of ultrahigh-purity helium and oxygen. These gases were used without further purification. Low pressure measurements were made with a capacitance manometer calibrated against a dibutyl phthalate manometer. High pressure measurements (5-800 torr) were made with a two turn precision Bourdon gauge.

TABLE I. Rate measurements at 298°K using resonance fluorescence-flash photolysis.

| C <sub>2</sub> H <sub>4</sub><br>(mtorr) | O <sub>2</sub><br>(torr) | Total pressure<br>(torr He) | Flash energy<br>(J) | First-order<br>rate constant<br>$k_{\text{exptl}}$<br>(sec <sup>-1</sup> ) | Bimolecular<br>rate constant<br>$k \times 10^{13}$ (cm <sup>3</sup><br>molecule <sup>-1</sup> ·sec <sup>-1</sup> ) |
|--|--------------------------|-----------------------------|---------------------|--|--|
| 5.27                                     | 1                        | 40                          | 100                 | 204  | 8.59   |
| 15.8                                     | 1.7                      | 40                          | 200                 | 508  | 8.55   |
| 15.8                                     | 0.5                      | 40                          | 200                 | 493  | 7.90   |
| 15.8                                     | 1.0                      | 40                          | 100                 | 474  | 8.13   |
| 15.8                                     | 1.0                      | 40                          | 400                 | 481  | 8.28   |
| 15.8                                     | 2.85                     | 40                          | 400                 | 525  | 8.53   |
| 15.8                                     | 0.3                      | 40                          | 100                 | 478  | 8.10   |
| 15.8                                     | 1.0                      | 5                           | 100                 | 647  | 8.19   |
| 15.8                                     | 1.0                      | 120                         | 100                 | 473  | 8.00   |
| 15.8                                     | 0.3                      | 120                         | 100                 | 483  | 8.85   |
| 15.8                                     | 0.6                      | 120                         | 200                 | 492  | 8.73   |
| 15.8                                     | 1.0                      | 240                         | 100                 | 575  | 8.06   |
| 26.4                                     | 0.5                      | 40                          | 200                 | 787  | 8.63   |
| 52.7                                     | 1.0                      | 40                          | 100                 | 1430   | 8.00   |
| 15.8                                     | 1.5                      | 40(N <sub>2</sub> )         | 45                  | 445  | 7.60   |
| 21.1                                     | 0.5(SO <sub>2</sub> )    | 20(Ar)                      | 65                  | 650  | 8.42   |
| 0  | 1                        | 5                           | 100                 | 240  |  |
| 0  | 1                        | 40                          | 100                 | 70   |  |
| 0  | 1                        | 120                         | 100                 | 68   |  |
| 0  | 1                        | 250                         | 100                 | 113  |  |
| 0  | 1.5                      | 40(N <sub>2</sub> )         | 100                 | 55   |  |
| 0  | 0.5(SO <sub>2</sub> )    | 20(Ar)                      | 100                 | 76   |  |

## RESULTS

The results of this study are presented in Tables I-IV. The data of Tables I and II were taken at the University of Maryland, and the data of Tables III and IV were taken at the National Bureau of Standards. In Table I are listed the results at room temperature using the flash photolysis-resonance fluorescence apparatus. Rate constants were measured over a pressure range of 5-240 torr, an ethylene partial pressure of 5.27-52.7 mtorr, and a 40-fold change in initial atomic-oxygen concentration. Within the experimental error of the technique, the rate constant was found to be invariant under all conditions. Typical multichannel analyzer curves for runs with and without ethylene are shown in Fig. 2.

Rate measurements at several different temperatures are given in Table II. A plot of  $\log k$  vs  $10^3/T$  (Fig. 3) shows that over the temperature range 232-500°K there is a simple straight line Arrhenius fit to the data. The precision of each measurement is indicated by the attached error bars and is  $\pm 5\%$  at worst.

Table III shows the results from this study using the flash photolysis-kinetic absorption technique. Also included are the results obtained employing resonance fluorescence detection. These measurements were all performed at 50 torr total pressure using He as a diluent gas and at room temperature, but the ethylene partial

pressure was varied from 35.8 to 128 mtorr. With this system also, no change in the rate constant was observed over the given experimental conditions. Only the lowest energy level ( $J=2$ ) of the OI triplet at 1302 Å was used in the absorption measurements. The atom concentrations here were calculated from the known oscillator strength for the  $J=2$  line of the oxygen triplet.<sup>22</sup> In the course of this work, it was observed that the unresolved higher energy  $J$  states of the oxygen triplet ( $J1, O$ ) from the resonance lamp were only slightly absorbed by the oxygen atoms produced in the reaction cell, when sampled about 100  $\mu\text{sec}$  after the flash—the usual delay time used in these experiments. This indicates that most of the oxygen atoms in the reaction cell after this time interval are in the  $J=2$  ground state, as would be expected for a thermal distribution.

Results from the discharge flow system are presented in Table IV. These experiments were carried out at a total pressure of from 1.3 to 2.3 torr, and flow velocities from 650 to 1630 cm sec<sup>-1</sup>. The ratio of the atomic-oxygen to ethylene concentration was varied from about 0.8 to 6.6 at 307°K with no apparent change in the rate constant.

From Tables I, III, and IV, it can be seen that within the experimental errors of the three techniques, the value of the absolute rate constant for reaction of O(<sup>3</sup>P) with C<sub>2</sub>H<sub>4</sub> is  $8.44 \times 10^{-13}$  cm<sup>3</sup> molecules<sup>-1</sup>·sec<sup>-1</sup> at 298°K. Using the temperature data from the resonance

TABLE II. Rate measurements using flash photolysis-resonance fluorescence.

| Temperature<br>(°K) | C <sub>2</sub> H <sub>4</sub><br>(mtorr) | O <sub>2</sub><br>(torr) | Total pressure<br>(torr He) | Flash energy<br>(J) | First-order<br>rate constant<br><i>k</i> <sub>exptl</sub> (sec <sup>-1</sup> ) | Bimolecular<br>rate constant<br><i>k</i> × 10 <sup>13</sup> (cm <sup>3</sup><br>molecule <sup>-1</sup> ·sec <sup>-1</sup> ) |
|---------------------|--|--------------------------|-----------------------------|---------------------|--|---|
| 232                 | 0  | 1.5                      | 40                          | 60                  | 84   |   |
| 232                 | 15.8                                     | 1.5                      | 40                          | 60                  | 395  | 4.72  |
| 232                 | 26.3                                     | 1.5                      | 40                          | 60                  | 571  | 4.46  |
| 256                 | 0  | 1.5                      | 40                          | 50                  | 82   |   |
| 256                 | 5.26                                     | 1.5                      | 40                          | 50                  | 192  | 5.83  |
| 256                 | 15.8                                     | 1.5                      | 40                          | 50                  | 422  | 5.71  |
| 256                 | 26.3                                     | 1.5                      | 40                          | 50                  | 626  | 5.49  |
| 284                 | 0  | 1.5                      | 40                          | 60                  | 71   |   |
| 284                 | 15.8                                     | 1.5                      | 40                          | 60                  | 469  | 7.43  |
| 341                 | 0  | 1.5                      | 40                          | 100                 | 80   |   |
| 341                 | 10.5                                     | 1.5                      | 40                          | 100                 | 381  | 10.1  |
| 341                 | 15.8                                     | 1.5                      | 40                          | 100                 | 571  | 11.0  |
| 379                 | 0  | 1.5                      | 40                          | 50                  | 106  |   |
| 379                 | 5.26                                     | 1.5                      | 40                          | 50                  | 259  | 11.5  |
| 379                 | 26.3                                     | 1.5                      | 40                          | 50                  | 830  | 10.8  |
| 379                 | 52.6                                     | 1.5                      | 40                          | 50                  | 1734   | 12.1  |
| 398                 | 0  | 1.5                      | 40(N <sub>2</sub> )         | 50                  | 67   |   |
| 398                 | 15.8                                     | 1.5                      | 40(N <sub>2</sub> )         | 50                  | 549  | 12.5  |
| 398                 | 31.6                                     | 1.5                      | 40(N <sub>2</sub> )         | 50                  | 1055   | 12.8  |
| 406                 | 0  | 1.5                      | 40                          | 100                 | 131  |   |
| 406                 | 5.26                                     | 1.5                      | 40                          | 100                 | 308  | 14.2  |
| 406                 | 15.8                                     | 1.5                      | 40                          | 100                 | 596  | 12.5  |
| 451                 | 0  | 1.5                      | 40                          | 100                 | 250  |   |
| 451                 | 15.8                                     | 1.5                      | 40                          | 100                 | 764  | 15.2  |
| 500                 | 0  | 1.5                      | 40                          | 100                 | 422  |   |
| 500                 | 15.8                                     | 1.5                      | 40                          | 100                 | 1090   | 18.1  |

fluorescence kinetic measurements (Fig. 2), an Arrhenius expression can then be written of the form:  $k = 5.42 \pm 0.30 \times 10^{-12} \exp[(-1130 \pm 32 \text{ cal mole}^{-1})/RT]$  cm<sup>3</sup> molecules<sup>-1</sup>·sec<sup>-1</sup>. The uncertainties given are standard errors of the reported values based on a least squares treatment.

## DISCUSSION

In Fig. 3, rate constants measured in this work and those reported by other investigators are presented with an Arrhenius line drawn to fit the data of the present work. Not included in this graph are rate constants derived from relative rate measurements or from discharge flow experiments which depend upon the analysis of final reaction products to derive rate parameters.<sup>6</sup> The latter results fall about two orders of magnitude below those presented here. The data of Atkinson and Cvetanović<sup>2b</sup> appeared in the literature subsequent to the preparation of this figure.

From Fig. 3, it can be seen that the rate measurements of Westenberg and de Haas<sup>10</sup> show the greatest deviation from the present work at the higher temperatures. Using their data over the temperature range of 195–715°K, a two-component curve can be drawn which

yields activation energies at high temperatures of 2.8 kcal mole<sup>-1</sup> and at low temperatures of 1.1 kcal mole<sup>-1</sup>. In these measurements, a discharge-flow system with ESR detection was employed. Using this technique, absolute rate constants can be calculated from the experimental data only after the chain length for removal of atomic oxygen is known over the entire temperature range studied. The rate constants reported in the study of Westenberg and deHaas were based on a stoichiometric factor  $n = \Delta[\text{O}]/\Delta[\text{C}_2\text{H}_4]$  (related to, but not necessarily equal to, the chain length) of 2, as measured at 195, 298, and 550°K. The experimental conditions under which this factor,  $n$ , was obtained (excess C<sub>2</sub>H<sub>4</sub>) differed from the conditions under which the rate measurements were made (large excess of C<sub>2</sub>H<sub>4</sub>). It would appear that if the value of  $n$  were in error it would necessarily be too low (compared to the correct chain length) due to possible consumption of C<sub>2</sub>H<sub>4</sub> by other radical species. This would be particularly true at higher temperatures, where higher activation energy processes would be more important. A comparison of rate data from the present work with that of Westenberg and de Haas shows, in fact, good agreement at low temperatures—both giving activation energies of 1.1 kcal mole<sup>-1</sup>. It is quite possible, there-

fore, that the higher activation energy arrived at by Westenberg and de Haas is due to the presence of complex side reactions giving too low a value of  $n$  at elevated temperatures. Such reactions are presumably less important at the lower temperatures, and a proper value of  $n$  was used.

At room temperature and 220°K, the rate data of Elias,<sup>11</sup> shown also in Fig. 3, agree well with the work reported here. At higher temperatures, these rate constants are somewhat higher than those predicted from the present work. In Elias' measurements a discharge

TABLE III. Rate measurements at 298°K using flash photolysis-kinetic absorption spectroscopy and flash photolysis-resonance fluorescence.

| C <sub>2</sub> H <sub>4</sub><br>(mtorr) | O <sub>2</sub><br>(torr) | [O] <sub>0</sub><br>(mtorr) | Flash<br>energy<br>(J) | 10 <sup>13</sup> k<br>(cm <sup>3</sup> mole-<br>cule <sup>-1</sup> ·sec <sup>-1</sup> ) |
|--|--------------------------|-----------------------------|------------------------|---|
| Absorption                               |                          |                             |                        |   |
| 49.17                                    | 0.85                     | 0.2                         | 400                    | 9.10±1.00 <sup>a</sup>  |
| 49.17                                    | 0.85                     | 0.2                         | 400                    | 8.83±0.79   |
| 39.35                                    | 0.85                     | 0.2                         | 400                    | 9.13±1.00   |
| 39.35                                    | 0.85                     | 0.2                         | 400                    | 8.15±1.06   |
| Fluorescence                             |                          |                             |                        |   |
| 35.81                                    | 1.0                      | 0.3                         | 500                    | 8.62±0.21   |
| 35.81                                    | 1.0                      | 0.3                         | 500                    | 8.85±0.20   |
| 35.81                                    | 1.0                      | 0.3                         | 500                    | 8.59±0.12   |
| 66.50                                    | 1.0                      | 0.3                         | 500                    | 8.56±0.28   |
| 66.50                                    | 1.0                      | 0.3                         | 500                    | 8.88±0.24   |
| 66.50                                    | 1.0                      | 0.3                         | 500                    | 7.65±0.18   |
| 97.19                                    | 1.0                      | 0.3                         | 500                    | 8.44±0.33   |
| 97.19                                    | 1.0                      | 0.3                         | 500                    | 8.63±0.31   |
| 97.19                                    | 1.0                      | 0.3                         | 500                    | 8.39±0.21   |
| 127.9                                    | 1.0                      | 0.3                         | 500                    | 8.12±0.41   |
| 127.9                                    | 1.0                      | 0.3                         | 500                    | 8.17±0.49   |
| 127.9                                    | 1.0                      | 0.3                         | 500                    | 7.79±0.31   |
| 61.38                                    | 0.15                     | 0.04                        | 400                    | 8.69±0.43   |
| 61.38                                    | 0.15                     | 0.04                        | 400                    | 7.61±0.30   |
| 122.76                                   | 0.30                     | 0.08                        | 400                    | 9.51±0.67   |

<sup>a</sup> The errors cited are estimates of the standard deviation  $\sigma$ .

flow system was employed in which the atomic-oxygen concentration was monitored using the O+NO chemiluminescence reaction. Sufficient ethylene was added in these experiments to completely consume the atomic oxygen. The excess ethylene concentration was then determined by being frozen in a cold trap at the end of the reaction zone. By determining the ethylene concentration at the beginning and end of the reaction zone (that is, the amount trapped out in a given period of time with the discharge off and the amount with the discharge on), and the decay of atomic oxygen down the reaction tube, the rate constant could be determined. The procedure for determining the rate constant as-

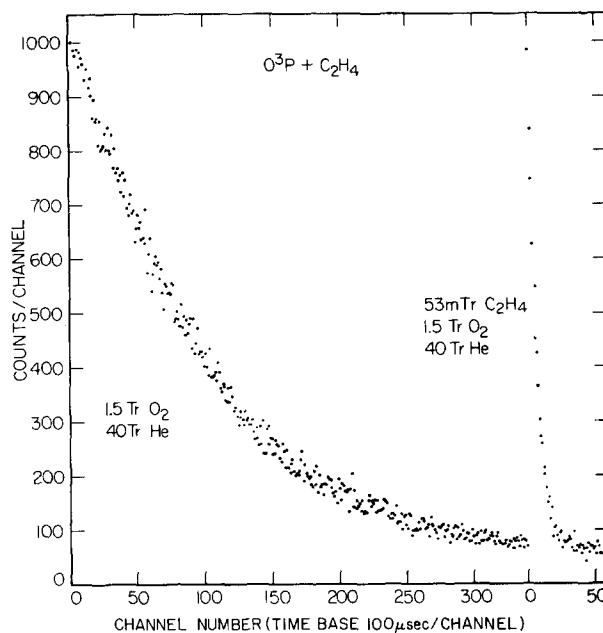


FIG. 2. Typical O-atom decay curves,  $T=379^\circ\text{K}$ . (a) Flash energy is 50 J,  $[\text{O}_2]=1.5$  torr,  $P=40$  torr, 150 flashes. (b) Flash energy is 50 J,  $[\text{C}_2\text{H}_4]=52.6$  mtorr,  $[\text{O}_2]=1.5$  torr,  $P=40$  torr, 340 flashes.

sumes that ethylene is lost only through reaction with atomic oxygen. Secondary reactions which consume ethylene would result in an apparent rate constant higher than the correct value. As discussed above, the error would be expected to be greater at higher temperatures, which is consistent with the direction of the deviation of Elias' data from the Arrhenius line reported here.

The high-temperature (1400–1860°K) value of Fenimore and Jones lies about an order of magnitude above the extrapolated value from this work. Their value was obtained by following the decay of ethylene in a pre-

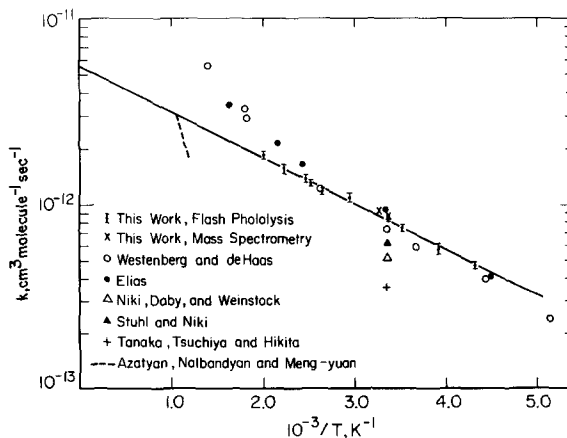


FIG. 3. Arrhenius plot of the rate constant for the reaction of atomic oxygen with ethylene.

TABLE IV. Rate measurements using discharge flow-mass spectrometer.

| Temperature<br>(°K) | Total pressure<br>(torr) | Velocity<br>(cm sec <sup>-1</sup> ) | [C <sub>2</sub> H <sub>4</sub> ] <sub>0</sub><br>(mtorr) | [O] Av<br>(mtorr) | 10 <sup>13</sup> k (cm <sup>3</sup><br>molecules <sup>-1</sup> ·sec <sup>-1</sup> ) |
|---------------------|--------------------------|-------------------------------------|--|-------------------|---|
| 298                 | 1.30                     | 1160                                | 0.21   | 0.63              | 9.26  |
| 298                 | 2.27                     | 660                                 | 0.25   | 0.46              | 8.07  |
| 307                 | 1.12                     | 1330                                | 0.14   | 0.88              | 7.77  |
| 307                 | 1.36                     | 1060                                | 0.13   | 1.44              | 9.86  |
| 307                 | 2.11                     | 670                                 | 0.16   | 1.05              | 9.36  |
| 307                 | 1.90                     | 650                                 | 0.44   | 1.05              | 9.28  |
| 307                 | 1.50                     | 1120                                | 0.42   | 0.34              | 9.45  |
| 307                 | 1.71                     | 1630                                | 0.45   | 0.59              | 9.53  |
| 307                 | 1.74                     | 1240                                | 0.39   | 0.60              | 9.85  |

mixed ethylene-oxygen-hydrogen flame. The procedure rests on many assumptions, and the breakdown of any of these assumptions could lead to the observed differences. The rate constants obtained by Azatyen, Nalbendyan, and Meng-yuan<sup>5</sup> using the first explosion limit of H<sub>2</sub>-O<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> and CO-O<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> mixtures agree qualitatively with the results reported here. The derived activation energy of 8100 cal mole<sup>-1</sup>, however, is considerably higher than the present value of 1130 cal mole<sup>-1</sup>.

There are several other values for the room-temperature rate constant that should be mentioned. Niki, Daby, and Weinstock<sup>9</sup> and Tanaka, Tsuchiya, and Hikita<sup>8</sup> employed discharge flow systems coupled to time-of-flight mass spectrometers to obtain values of *k* some 40% lower than reported here. Brown and Thrush<sup>4</sup> used an ESR flow system, similar to that of Westenberg and de Haas<sup>16</sup> for the room-temperature study of the atomic-oxygen-ethylene rate constant. Their experimental conditions were not clearly stated in their paper and, therefore, the chain-length value which should be used to derive the rate constant is not apparent. This problem has been discussed by Westenberg.<sup>10</sup> The difference between our result and those of the flow systems are possibly within the experimental uncertainty of the latter.

A recent investigation by Stuhl and Niki<sup>13</sup> using a flash photolysis-chemiluminescent method resulted in a rate constant about 25% below that reported here. A study by Atkinson and Cvetanović<sup>2b</sup> employing a similar chemiluminescent O-atom detection system coupled with a modulated atom source yielded a rate constant some 20% below that of Stuhl and Niki.<sup>13</sup> The expected error associated with these studies—added to the uncertainty of the present data—is less than the difference between the two sets of measurements at 298°K. In view of the expected accuracy of the techniques, a set of experiments was performed to determine the cause of this discrepancy.

The NBS apparatus was modified to permit O-atom monitoring by the O+NO+M chemiluminescent re-

action, and the experiments of Stuhl and Niki<sup>13</sup> were repeated. A mixture consisting of 250 mtorr NO, 0-75 mtorr C<sub>2</sub>H<sub>4</sub>, and 10 torr He was flash photolyzed, and the O-atom concentration was monitored by the NO<sub>2</sub> emission at 6100 Å via an interference filter (half-width is 75 Å, peak transmission at 6080 Å) coupled to an EMI 9558 photomultiplier. The pulse counting facilities of the previous experiments were employed. A rate constant of 6.0×10<sup>13</sup> cm<sup>3</sup> molecules<sup>-1</sup>·sec<sup>-1</sup> was obtained at 298°K, in excellent agreement with the value 6.3×10<sup>13</sup> obtained by Stuhl and Niki.<sup>13</sup> These same experiments were repeated with the addition of 0.1-1.0 torr of O<sub>2</sub> to the reaction mixture. The signal increased significantly as expected due to the increased O-atom concentration, however, the over-all sensitivity remained lower than in a comparable resonance fluorescence experiment. The measured atom lifetime decreased due to the O+O<sub>2</sub> reaction, but when the first-order rate constant was corrected for this additional loss mechanism, the bimolecular rate constant for reaction of O with C<sub>2</sub>H<sub>4</sub> remained unchanged at 6.0×10<sup>13</sup> cm<sup>3</sup> molecules<sup>-1</sup>·sec<sup>-1</sup>. These latter experiments clearly overlap the atom concentration range employed in the resonance fluorescence experiments and would seem to refute any arguments that the resonance fluorescence and absorption experiments require stoichiometric correction. (The absence of any change in *k* over the wide range of O-atom concentration employed in our studies also serves to argue against the need for stoichiometric correction.)

One might question whether the low value for *k* obtained with NO present is due to the free radical scavenging ability of the NO thereby eliminating any atom-radical reactions. The experiments without NO (using O<sub>2</sub> as the atom source) might then suffer from the poorer scavenging ability of the O<sub>2</sub> and would require some stoichiometric correction. If this were the case, however, one would have expected a change in *k* with atom concentration in our experiments. Nevertheless, as further proof, the University of Maryland System was used to perform several resonance fluorescence

experiments using  $\text{SO}_2$  as the O-atom source. An  $\text{SO}_2$  pressure of 0.5 torr was employed to obtain a 298°K value for  $k$  of  $8.42 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \cdot \text{sec}^{-1}$  in excellent agreement with the  $\text{O}_2$  work. We would have expected a higher rate constant if atom-radical reactions were important since  $\text{SO}_2$  is a much poorer scavenger than  $\text{O}_2$ .

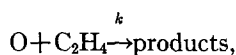
Finally, the NBS system was employed to conduct resonance fluorescence experiments under identical flash conditions and reaction mixture concentrations ( $\text{NO} + \text{O}_2 + \text{C}_2\text{H}_4 + \text{He}$ ) as were used in our chemiluminescence experiment. A  $k$  value of  $8.0 \pm 0.5 \times 10^{-13}$  was obtained. All the results, therefore, indicate that the O-atom-ethylene system generates a fluorescence in the presence of NO other than that due to  $\text{O} + \text{NO} + \text{M}$ . Such fluorescence, detectable at 6100 Å would give rise to an observed O-atom lifetime which was too long, and hence, a rate constant which was too small.

As a further check on the reliability of the resonance fluorescence measurements, several other possible sources of systematic error were considered. By carrying out experiments in three different laboratories, the possibility of systematic errors due to incorrect calibration procedures in one laboratory was minimized. The calibration of the capacitance manometer was checked frequently, and very little drift was observed. Gas mixtures were prepared over wide concentration ranges with no effects on the observed rate constant noted; it is therefore unlikely that any significant loss of reactant gas on the walls of the mixing bulbs occurred.

The time base of the multichannel analyzer was checked against a crystal-controlled clock, and the linearity was checked using a frequency generator. With the analyzer set in the 100- $\mu\text{sec}$ /channel position, the time base was shown to be  $103 \pm 1 \mu\text{sec}$ . All rate parameters reported in this work are based on this value of 103  $\mu\text{sec}$ /channel.

Kinetic runs using nitrogen as a diluent gas were performed at room and elevated temperatures, and the results agreed with those found using helium as a diluent gas. This implies the absence of effects due to thermal transport or quenching of excited states.

The effect of secondary O-atom reactions on the measured rate constant can be assessed using the simple mechanism,



$$k = 8.4 \times 10^{-13} \text{ cm}^3/\text{molecules} \cdot \text{sec},$$



$$k_p = 1 \times 10^{-10} \text{ cm}^3/\text{molecules} \cdot \text{sec}.$$

Near-collision frequency has been selected for  $k_p$  to ensure a "worst-case" calculation. At an ethylene concentration of 100 mtorr and an O-atom concentration

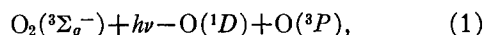
of 0.2 mtorr, the apparent rate constant would be  $1 \times 10^{-12} \text{ cm}^3/\text{molecules}^{-1} \cdot \text{sec}^{-1}$  corresponding to a chain length  $n$  of 1.25. With 50 mtorr  $\text{C}_2\text{H}_4$ , the chain length would be 1.5. Under these conditions, then, the apparent rate constant would be a function of the ethylene concentration at a fixed O-atom concentration. In general the chain length (i.e., the proper stoichiometric correction) is strongly dependent on the  $[\text{C}_2\text{H}_4]/[\text{O}]_0$  ratio. As demonstrated in an earlier publication,<sup>16</sup> the absence of a change in observed rate coefficient with this ratio indicates either the absence of secondary reactions ( $n=1$ ) or a higher integral value of  $n$ . In the flash photolysis-resonance fluorescence photolysis experiments the ethylene concentration was varied by a factor of 20 with no change observed in the rate constant. Thus, in these experiments the chain length correction factor,  $n$ , would necessarily have to be an integral number either 1 or 2. Under the conditions shown in Table III, however,

$$10^2 < [\text{C}_2\text{H}_4]/[\text{O}]_0 < 3 \times 10^3,$$

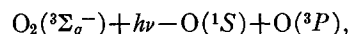
$k_p$  would have to be approximately  $2 \times 10^{-9} \text{ cm}^3/\text{molecular} \cdot \text{sec}$  for  $n=2$ . Such a value for  $k_p$  is somewhat greater than the gas kinetic collision frequency and suggests that the rate of loss of  $\text{O}(^3P)$  by secondary reactions is negligible under the conditions of the present study (i.e.,  $n=1$ ).

In the above calculation, the possible effects of secondary reactions involving intermediate reaction products, such as  $\text{CH}_3$ ,  $\text{CHO}$ , etc., were considered. Since each sample was flashed several times, the possibility exists that stable products, such as  $\text{CH}_2\text{O}$ , could also systematically alter the measured rate constants. In the resonance fluorescence experiments, however, by the end of a single run, the correction for the reaction of atomic oxygen with formaldehyde (assuming unit production of formaldehyde and a net over-all conversion of ethylene of 5%) would have been less than 1%. Again, any such effect outside of our precision ( $\sim 3\%$ ) would have been observed as the reactant concentrations were varied. As seen in Table I no effect was observed.

In the flash photolysis of molecular oxygen the most likely primary process is<sup>23</sup>



which has an onset at 1759 Å. The spin-forbidden production of two  $^3P$  atoms above 1759 Å is a very minor process. Below 1342 Å, the process,



is also possible. In these experiments, delay times of 100–200  $\mu\text{sec}$  (following the photoflash) were employed before the atom decay was observed. In this time, the very rapid deactivation rate for  $\text{O}(^1D)$ <sup>24</sup> resulted in the complete removal of this species. The



deactivation rate of  $O(^1S)$ , however, is somewhat slower.<sup>24</sup> Therefore, the slow deactivation of  $^1S$  to  $^3P$  during an experiment would lead to an  $O(^3P)$  decay which was too slow. To examine this possibility, experiments were carried out using a sapphire window, which blocks radiation below 1410 Å, on the flash lamp. Within the experimental error, no change in the rate constant was observed, indicating that the production of  $O(^1S)$  is not an important process in this system. The deactivation of  $O(^1D)$  in the presence of  $O_2$  and He, where  $O_2$  is the principal deactivating species, would also result in the production of  $O_2(^1\Sigma_g^+)$ . Since only  $O(^3P)$  is being followed [the photocathode used being insensitive to the 7596-Å emission of  $O_2(^1\Sigma)$ ] the presence of  $O_2(^1\Sigma)$  should not have influenced the reported results. This was shown to be the case in those experiments where  $N_2$  was used as the diluent gas rather than He. In these experiments, most of the deactivation of  $O(^1D)$  was by  $N_2$ ,<sup>24</sup> and very little  $O_2(^1\Sigma)$  was formed. As seen in Tables I and II, the results of the  $N_2$  and He experiments agree indicating no systematic influence of  $O_2(^1\Sigma)$  on the observed kinetics.

Another possible source of error in the resonance fluorescence measurements is fluorescence resulting from the direct excitation of  $C_2H_4$  or  $O_2$  by either the photoflash or the resonance lamp. However, since photocathodes were used having long-wavelength cut-offs of 1350 Å (tungsten) and  $\sim 1850$  Å (CuI), most of the natural fluorescence from these compounds would have been only weakly detected. Any continuous fluorescence signal resulting from the cw operated resonance lamp would appear as a part of the background signal and would have been corrected for as outlined previously in the experimental section. In addition, the 100–200- $\mu$ sec delay between the photoflash and the start of kinetic sampling would exclude the possibility of a fluorescence signal being produced by the photoflash itself. This was checked several times by looking at the signal produced by approximately 100 flashes of a standard reaction mixture with the resonance lamp off. No significant signal was observed.

Finally, the excellent agreement between fluorescence and absorption measurements negates any possibility that the fluorescence runs had a signal contribution due to something other than oxygen atoms.

### SUMMARY

Rate constants for the reaction of atomic oxygen with ethylene have been measured using three different experimental techniques in three different laboratories.

Experimental conditions have been varied over a wide range in an effort to detect possible complications in the rate measurement. No such complications were found, and results of the different techniques were in complete agreement. The importance of secondary reactions was assessed and their contribution found to be insignificant. Rate constants as a function of temperature could be fitted over the entire range to a simple Arrhenius expression of the form,

$$k = 5.42 \pm 0.30 \times 10^{-11} \exp[(-1130 \pm 32 \text{ cal mole}^{-1})/RT] \\ \times \text{cm}^3 \text{ molecules}^{-1} \cdot \text{sec}^{-1}.$$

\* Acknowledgement is made by this author to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

† The research carried out at the University of Maryland is part of a thesis to be submitted to the Faculty of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

‡ Supported in part by the Measures for Air Quality Program of the National Bureau of Standards.

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