Direct Measurement of the Thermal Rate Coefficient for Electron Attachment to Ozone in the Gas Phase, 300–550 K: Implications for the Ionosphere

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Attachment of thermal electrons to O_3 was studied in 133 Pa He between 300–550 K; the process is extremely inefficient. The rate coefficient increases sharply with temperature from 0.9 to 5×10^{-11} cm^3 s^{-1} ($\pm 30\%$) and comparison to kinetic energy measurements suggests internal energy can drive the reaction. These determinations account for competing processes of diffusion, recombination, and electron detachment reactions, and imply that no significant zero-energy resonance cross section exists, contradicting recent electron-beam results that call for substantial revision of ionospheric models.

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A narrow but strong zero-energy resonance was observed and reported in this journal [1] and elsewhere [2] for electron attachment to ozone in experiments using a high-resolution trochoidal electron spectrometer. These data contradict early swarm [3] and drift tube work [4] that helped form the basis of current stratospheric and ionospheric chemistry models as well as with more recent beam experiments [5,6]. At issue is the role electron attachment to ozone plays in forming negative ions in the atmosphere. Before the report of Senn *et al.* [1,2] it was believed that three-body associative electron attachment to O_2 is the only significant chemical reaction initiating negative ion formation in both the stratosphere and the *D* region of the ionosphere where electron temperatures are in the 190–290 K range [7,8]. Measurements of direct (two-body) electron attachment to ozone at low energy indicated that it is very inefficient [3,4] and so would not compete with the three-body reaction in these regions. Other recent investigations of this reaction, primarily focusing on interactions at higher energy, do not contradict the conclusions of the earlier work while adding greatly to our understanding of this reaction [9–12]. In contrast, the results of Senn *et al.* [1,2] imply that binary electron attachment to ozone is a comparable source of negative ions throughout the stratosphere and *D* region of the ionosphere (estimated to have an average relative rate of 0.6–6 compared to three-body attachment to O_2 for 50–80 km altitude, respectively [13,14]). Furthermore, assessing the importance of this reaction in the atmosphere as well as in other environments (such as electrical discharges), requires knowledge of its temperature dependence. The only data available are from drift tube [4] and beam experiments [1,2,7,8], in which electron kinetic energy is varied but the rovibrational energy of the ozone is fixed. Electron temperature dependences are derived from these data by integrating over the electron energy distribution. Two completely different pictures emerge from the earlier studies [4,7,8] and the new work of Senn *et al.* [1,2], i.e., the earlier work predicts the rate coefficient has a positive electron temperature dependence while that of Senn *et al.* [1,2] predicts a negative temperature dependence in the 10–1000 K electron temperature range. Because of the importance of accurately knowing the kinetics of thermal electron attachment to ozone, and the ability of the flowing afterglow Langmuir probe (FALP) technique to directly measure the thermal rate coefficient for this reaction, we undertook the present study of the this reaction over the available temperature range of 300–550 K. The present study is the first investigation of the thermal rate coefficient for this reaction over this temperature range and the first study to quantitatively account for secondary reactive detachment reactions in its analysis.

The FALP method [15–17] and the Air Force Research Laboratory apparatus [18] have been described thoroughly in the literature. Briefly, the FALP consists of a fast-flowing electron/He$^+$, Ar$^+$ plasma to which an attaching gas is added at a point after the plasma has thermalized. The attaching gas causes the electron density n_e in the plasma to decay faster than by ambipolar diffusion alone. A cylindrical Langmuir probe is moved along the axis of the FALP flow tube in order to map out the change in n_e with distance (and equivalently, with time). An rf quadrupole mass spectrometer at the terminus of the flow tube identifies the ion product(s) formed.

Ozone was generated for the present work in a commercial ozonator, which gave ~5% O_3 in O_2 gas. The fraction of O_3 was determined accurately and continuously via UV absorption in a quartz cell, which was part of the neutral reactant inlet line, located just prior to the

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O_2/O_3 mixture entering the FALP [19]. Electron attachment to O_2 is negligible at the pressures and temperatures of the present experiments [14].

The electron attachment rate coefficient was obtained by fitting the electron density profile to the rate equations describing the processes affecting the electron density. In these experiments, the electron density along the length of the flow tube is reduced by three processes: diffusion, recombination, and electron attachment. The contribution to the electron decay from ambipolar diffusion was measured directly in the absence of the neutral reactant (O_3/O_2 mixture). The contribution to the decay from electron-positive ion recombination arises primarily from reaction of O_2^+ with electrons, where the O_2^+ ions are formed mainly from reaction of Ar^+ with O_2. The rate coefficient values for these reactions are well established [20,21] and were included in our model.

One additional process in the flow tube influences the electron density in the ozone electron attachment experiments at 300 K and to a lesser extent at higher temperatures, namely, the secondary reaction of the product ion O^- with ozone. This reaction has a minor channel forming free electrons [22] that decreases rapidly in importance above room temperature [23]. Recent measurements of the $O^- + O_3$ reaction rate coefficient and branching fraction temperature dependence [23] enable us to account accurately for this secondary process. We assume, based on thermochemistry and previous experiments, electron attachment to ozone forms only $O^- + O_2$ in our temperature range [3,7,8,24]. The mass spectra show almost exclusively O_3^- at the end of the flow tube due to a series of known fast ion-molecule reactions [19,20]. At room temperature, where the secondary reactive detachment process is most important and where the primary electron attachment rate coefficient is smallest, including this reactive detachment process leads to approximately a 20% increase in value of the best fit electron attachment rate coefficient. We note that release of electrons from this secondary ion-molecule reaction partly offsets electron-ion recombination losses at long times. (Collisional detachment of O_2^- formed in this secondary reaction is not included in our model because it is too inefficient [25] to compete with the efficient reaction of O_2^- with ozone [19] under our experimental conditions.)

Typical room temperature data (points) and our best fit line (solid black line) are shown in Fig. 1. An uncertainty of ±30% in the electron attachment rate coefficient leads to the bracketing dashed lines. For comparison, the attenuation of the electron density arising from diffusion alone and diffusion and recombination combined are also shown.

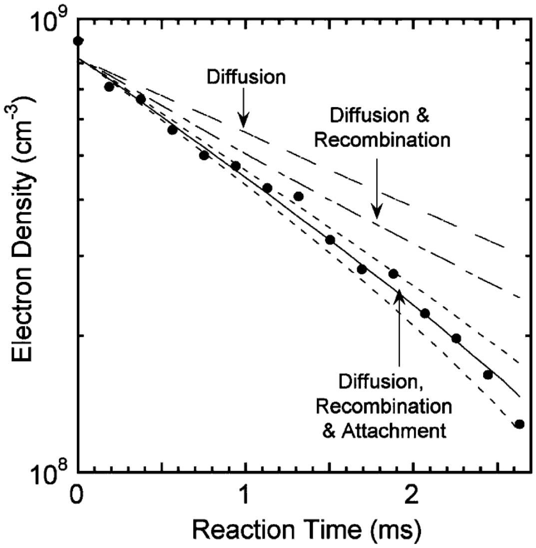

FIG. 1. Plot of the electron density as a function of time in the flow tube where $t = 0$ is the reactant inlet position. Experimental data (●), best fit (solid line), with ±30% uncertainty in electron attachment rate coefficient (short-dashed lines). Also shown are the contributions to electron density decay arising from ambipolar diffusion (long-dashed line) and ambipolar diffusion and electron-ion recombination combined (long- and short-dashed lines).

The observed/"best fit" electron attachment rate coefficient includes electron attachment by ozone and any electron attachment processes arising from impurities in the neutral reactant flow. The major impurity in the O_3/O_2 flow is HNO_3 (as evidenced by a small NO_3^- peak in the mass spectrum which shifts to NO_2^- when the ozonator is turned off) [26,27]. Using the negative ion mass spectrum obtained in each experiment, we quantified the impurity contribution and used this value to correct the determined rate coefficient to reflect electron attachment to ozone only [28]. The correction ranged from 2%–27% in our experiments, corresponding to <0.006% HNO_3 in the O_3/O_2 flow. The electron attachment rate coefficients reported include this correction for impurities.

The present thermal rate coefficients for electron attachment to ozone over the temperature range of 300–550 K determined are presented in Table I. These results indicate that electron attachment to ozone over this temperature range is extremely inefficient with fewer than 1 in 10^4 collisions resulting in attachment at 300 K. Increasing gas temperature increases the rate coefficient and efficiency of this process. These results are compared with previous determinations in Fig. 2. The present results are

TABLE I. Thermal rate coefficients for electron attachment to ozone with an estimated uncertainty of ±30%.

Temperature (K)	Rate coefficient (10^{-12} cm^3 s^{-1})
300	9
383	15
467	32
550	51

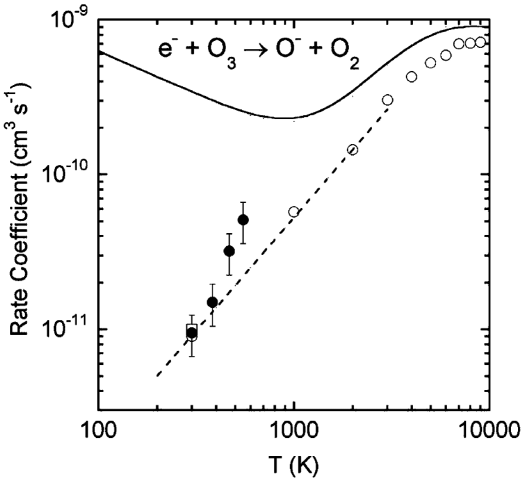

FIG. 2. Electron attachment rate coefficient versus temperature. Present results (●) and swarm upper limit of Fehsenfeld *et al.* [3] (□) are true thermal values. The remaing data are plotted versus electron temperature. The drift tube results of Stelman *et al.* [4] (dashed line) are derived from a least squares fit of the combined data for 200 and 300 K rovibrational temperature ozone reacting with energetic electrons. The electron beam results of Skalny *et al.* [8] (○) and Senn *et al.* [2] (solid line) were derived by those authors from measurements of the reaction cross section for 300 K rovibrational temperature ozone with energetic electrons.

in agreement with earlier swarm [3], drift tube [4], and electron-beam [8] data, but are in considerable disagreement with the most recent beam study that reports a large zero-energy resonance [1] from which they deduce electron attachment rate coefficients [2] that are over 5–30 times larger in the 300–550 K range. Fehsenfeld *et al.* [3], using a flowing afterglow apparatus, placed an upper limit on the 300 K rate coefficient of $<1 \times 10^{-11}$ cm^3 s^{-1} while Stelman *et al.* [4], using drift tube measurements, determined the electron temperature dependence of the reaction to be $9 \pm 2 \times 10^{-12}(T/300)^{1.46}$ cm^3 s^{-1}, represented as a dashed line in Fig. 2. The electron-beam results of Skalny *et al.* [6] using a trochoidal electron spectrometer, are in agreement with these swarm and drift tube data as well as with the present data. In contrast, the most recent results of Senn *et al.* [1,2] disagree strongly with these previous studies and the present work. It is important to note that the data presented by Skalny *et al.* [6] and Senn *et al.* [1,2] were collected with the same apparatus at the University of Innsbruck, where the latter experiments employed higher resolution and reported a narrow but large zero-energy resonance that was not observed in the earlier study. This zero-energy resonance is the cause of the dramatic differences in rate coefficients reported and shown in Fig. 2. More recently [29], the group has reevaluated their experiments leading to significantly modified (increased) electron attachment reaction cross sections at higher energy (>0.8 eV) but did not alter the lower energy values. While we do not know the cause of the enormous discrepancy between our data and those of Senn *et al.* [1,2], we do not believe that energy resolution alone can explain it. Our thermal experiments have very similar electron energy "resolution" (FWHM ranging from 46 meV at 300 K to 85 meV at 550 K) to those employed in the high-resolution experiments of Senn *et al.* [1,2]. Our experiments differ from the beam experiments in terms of the rovibrational temperature of the reactant ozone except at 300 K, where the disagreement is largest, the ozone rovibrational temperatures are identical. The Innsbruck group has recently identified autodetachment processes [30] in their experiment that can lead to specious zero-energy peaks, but it is not obvious that this explanation applies to the ozone experiments.

The temperature dependence determined in our experiments is similar to but steeper than that reported for the drift tube experiments of Stelman *et al.* [4] and the beam results of Skalny *et al.* [6] over the same temperature range. As mentioned above, these experiments differ from the present ones in that the ozone rovibrational temperature is held constant when the electron temperature is increased. The temperature dependence expression of Stelman *et al.* [4] plotted in Fig. 2, is derived from a least squares fit of the combined data for 200 and 300 K rovibrational temperature ozone reacting with energetic electrons while the data for Skalny *et al.* [6] are for 300 K rovibrational temperature ozone. The significantly larger rate coefficients determined at 467 and 550 K in the present work suggest that internal energy increases the rate coefficient for electron attachment. While most of the internal energy is rotational over the explored temperature range, it is worth noting that the vibrational contribution is rapidly increasing. The percent of vibrationally excited O_3 increases from 4 at 300 K to 26 at 550 K and the percent of ozone with excitation in the asymmetric stretch (reaction coordinate) increases from <1 to 6 over this temperature range [31]. Because of the combined uncertainties of the different data sets it is not possible to definitively determine whether both rotational and vibrational energies contribute to the observed rate coefficient. To further investigate the internal energy effects on the rate of this reaction, one should study the reaction at temperatures >550 K (not possible in our apparatus) where the attachment rate coefficient would be larger.

We have measured the thermal rate coefficient for electron attachment to ozone over the temperature range of 300–550 K and find that this reaction is extremely inefficient. The rate coefficient increases with temperature from $9 \pm 3 \times 10^{-12}$ cm^3 s^{-1} at 300 K to $5 \pm 1 \times 10^{-11}$ cm^3 s^{-1} at 550 K. Our analysis, leading to these reported rate coefficients, improves on earlier swarm and drift tube work by quantitatively accounting for secondary ion-molecule electron detachment reactions. Comparison of the measured temperature dependence with electron energy dependences measured by others, suggests that internal energy can help fuel the reaction. Finally, our results indicate that no significant zero-energy resonance exists in the attachment cross section. Therefore, current ionospheric models of the stratosphere and *D* region that either ignore or treat electron attachment to ozone as a minor process need not be significantly modified. Models including ozone electron attachment at higher temperatures such as models of electrical discharges should be modified to reflect the temperature dependence determined in this work.

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