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Measurement of $O_2^+ + e^-$ Dissociative Recombination in Expanding Oxygen Flows

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The dissociative-recombination rate coefficient for the reaction $O_2^+ + e^- \xrightarrow[k_r]{} O + O$ has been measured in the invisid nozzle flow of a short-duration reflected-shock tunnel and found to be given by $k_r = (8 \pm 2) \times 10^{21}\ T_e^{-1.5}$ cm³/mole sec for an electron temperature range of approximately 1800°K to 5000°K. These experiments were performed in oxygen at equilibrium reservoir conditions of 4950°K and 25 atm pressure. Thin-wire Langmuir probes were used to measure the electron temperature and electron density on the nozzle centerline. The electron densities were simultaneously measured using microwave interferometers.

1. Introduction

PREVIOUS papers[1,2] by the authors have presented rate-coefficient data for the dissociative recombination (k_r) of NO^+ and N_2^+. The purpose of this paper is to present rate-coefficient data, obtained in the same manner, for the reaction

$$O_2^+ + e^- \underset{k_i}{\overset{k_r}{\rightleftharpoons}} O + O$$

It is typical of this class of reactions that the ionization and recombination rate coefficients are related to the local plasma conditions through the temperature, the ionization rate being dependent upon the heavy-particle translational temperature while the recombination rate depends mainly on the electron temperature. Both of these temperatures must be known in experiments to evaluate the recombination-rate coefficient.

Experimental data for the two-body dissociative recombination of O_2^+ for electron temperatures greater than 450°K are scarce, with only two points reported.[3,4] However, many data points have been reported at 300°K or slightly greater temperatures. Discharge tube measurements, the only ones available, of the dissociative recombination of O_2^+ have been complicated as a result of the reported[5] presence of O_3^+ in nontrivial quantities. Sayers[3] and Sayers and Kerr[4] provide the only reports of high-temperature experiments, reporting values at approximately 2000°K and 2600°K. They studied the electron-density decay in the afterglow of a discharge. A radio-frequency mass spectrograph was used to identify the ions present in the plasma and to confirm the absence of negative ions.

Anisimov, Vinogradov, and Golant[6] measured the dissociative recombination of O_2^+ by studying the electron-density decay, using a microwave cavity resonator, in the afterglow of a discharge tube. A pulsed electrode discharge was used to create the plasma in a long chamber, along the axis of which they placed a strong magnetic field in an attempt to limit the effects of diffusion.

Biondi, Connor, and Weller[7] and Kasner and Biondi[8] studied the afterglow of an arc discharge and obtained data points at 300°K that were in reasonably good agreement with the other 300°K data.

Holt[9] investigated the dissociative recombination of O_2^+ in the afterglow decay of a plasma created by an arc discharge. He worked in the pressure range 0.3 to 10 mm Hg and detected electron densities in the range 10^8 to 10^{11} e^-/cm^3. The electron losses due to recombination, diffusion, and attachment for 300°K electrons were separated according to the respective loss laws. The experimental value of the reaction rate constant was in good agreement with others available for 300°K.

In the present experiments, both the electron temperature and the electron density were measured in the expanding oxygen plasma. Then the recombination rate coefficient for the dominant reaction was adjusted until the calculated number density agreed with the probe and microwave-interferometer data. The measured electron-temperature history was used in calculating the variation of the number density along the nozzle. The relative importance of various reactions included in the reaction model was independently assessed. In Sec. 2 the experimental apparatus and procedure are briefly dis-

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cussed. The method of data analysis is described in Sec. 3 and the experimental results are discussed in Sec. 4.

2. Experimental Apparatus and Technique

A pressure-driven shock tube was used to produce a reservoir of high-temperature oxygen which was subsequently expanded in a conical nozzle. The test gas used in these experiments was UPC oxygen supplied by Air Products and Chemicals Inc. A chemical analysis of the gas indicated the following: 17 ppm nitrogen, carbon dioxide less than 0.5 ppm, carbon monoxide less than 1.0 ppm, nitrous oxide less than 0.1 ppm, methane less than 0.5 ppm, acetylene less than 0.05 ppm, total hydrocarbons less than 1 ppm, and 0.15 ppm of water. The shock tube was purged with approximately 5.0 torr of the test gas prior to each run.

The electron number densities were measured at 11.5, 21.5, and 31.5 in. from the nozzle throat, using microwave interferometers operating at frequencies of either 35 or 17 GHz. The interferometers are discussed in more detail in Ref. 13. One inch downstream of each microwave interferometer measuring station, thin-wire Langmuir probes were used on the nozzle centerline to measure the electron temperature and electron density. The electron density, electron temperature, and visible-radiation intensity were simultaneously measured in the nozzle for each experiment. Detailed discussion of the shock tube and nozzle measurements is given in Refs. 1, 13, and 14.

The probes used in these experiments were constructed by surrounding 0.004-in.-diam tungsten wires with a quartz envelope, leaving a nominal 0.400-in.-length of bare wire exposed. Immediately prior to each run, the probe was ultrasonically cleaned in a dilute solution of sodium hydroxide to remove the tungsten oxide.

Two different voltage sweep rates were applied to the probe in separate experiments conducted at each measuring station in order to obtain the probe data. The probe voltage was swept from -6 to $+1$ (relative to ground potential) and from -3 to $+0.5$ v in approximately 80 μsec. At the upstream station, where the electron density was in excess of 10^{10} e^-/cm^3, the electron temperature and electron density deduced from the probe data were independent of the voltage sweep rate. At the 22.5 and 32.5-in. stations, where the electron density was approximately 4×10^9 and 2×10^9 e^-/cm^3, respectively, higher electron temperatures (higher by about 50%) were obtained when the faster sweep rate was used. Electron-density measurements obtained with the probes at these stations with the faster sweep rates were substantially lower than those obtained with the microwave interferometers. At the 22.5-in. station, agreement would not be expected because of collision effects but at the 32.5-in. station the probe data should be in good agreement with the microwave-interferometer data. By reducing the sweep rate to the lower value, excellent agreement of the probe and interferometer data was obtained at the 32.5-in. measuring station. The Langmuir-probe data obtained with the lower sweep rate are felt to be correct. Sny and Greig[15] previously observed this same result when using too rapid a sweep rate at low number densities. It is clear that care must be taken when using voltage-swept probes when the electron density is less than 10^{10} e^-/cm^3. Furthermore, an independent measurement of electron density should be obtained whenever possible.

The quality of the Langmuir-probe and microwave-interferometer data records obtained in these experiments was comparable to that reported in Refs. 1 and 2 for air and nitrogen, respectively, as the test gas.

3. Technique Used to Determine Rate Coefficient

The procedure used to determine the reaction-rate coefficient from the experimental data has been described in detail in Ref. 2. Briefly, the correlation technique utilizes a nozzle-flow computer program[16] to compute the solution for the gasdynamic properties and chemical composition in the nonequilibrium expansion of an arbitrary gas mixture from an equilibrium reservoir state through a given nozzle geometry. It is thus possible to vary the rate coefficient of the dominant chemical reactions in order to match the calculated and measured nozzle electron densities. In performing these calculations, the variation of the electron temperature was prescribed on the basis of the Langmuir-probe measurements. The thermodynamic properties employed for these species are given in Ref. 16.

The impurities in the gas supply and those due to any leakage were found to have a negligible influence on the rate-coefficient determination for these experiments. The molecular nitrogen impurity was the one of most concern because of the potential importance of the NO^+ ion. On the basis of the known leak rate it was estimated that a nitrogen concentration of 25 ppm in the unshocked oxygen test gas would not be unreasonable. Nozzle-flow calculations were performed including the presence of nitrogen species and using the rate coefficient determined in Ref. 1 for the NO^+ deionization reaction. The presence of the nitrogen impurity was found to have a negligible influence on the determination of the rate coefficient for the reaction $O_2^+ + e^- \rightleftharpoons O + O$.

The chemical-kinetic model used in the data correlation is given in Table 1. As noted previously, reactions involving N_2, N, and NO and the reaction $NO^+ + e^- \rightleftharpoons N + O$ were initially included in the model but were subsequently deleted because they were unimportant for the conditions of interest. The importance of other relevant reactions also was investigated. Reaction 3 was found to be unimportant in the data correlation even if the rate coefficient (taken from Ref.17) was varied by a factor of ± 10. Reaction 5 also was found to be negligible compared with the deionization path of reaction 4. The rate coefficient for this reaction was taken from Makin and Keck.[18] Reactions 6-13 also were found to have a negligible influence on the $O_2^+ + e^-$ rate-coefficient determination. Rate coefficients for these reactions were taken from Sutton[19] and the DASA reaction rate handbook.[20] Additional negative-ion reactions were included in the initial model but were discarded because they were even less important than reactions 6-13.

The reaction remaining in the model after the above deletions was reaction 4, $O_2^+ + e^- \rightleftharpoons O + O$. As just discussed, the rate coefficient for the deionization of O_2^+ was evaluated at the electron temperature prescribed on the basis of the measured values. For the temperature histories used, the reverse rate of reaction 4 was always negligible at the point where the electron and heavy-particle translational temperature began to differ.

Table 1 Chemical-kinetic models used in data correlation

No.	Reaction	Forward rate-coefficient expression
1	$O_2 + O_2 \rightleftharpoons 2O + O_2$	$3.6 \times 10^{21} T^{-1.5} \exp(-117{,}960/T)$
2	$O_2 + O \rightleftharpoons 2O + O$	$2.1 \times 10^{18} T^{-0.5} \exp(-117{,}960/T)$
3	$O_2 + O^+ \rightleftharpoons O_2^+ + O$	1.2×10^{13}
4	$O_2^+ + e^- \rightleftharpoons O + O$	To be determined from this experiment
5	$O^+ + e^- + e^- \rightleftharpoons O + e^-$	$8.3 \times 10^{39} T_e^{-4.5}$
6	$O_2 + O + e^- \rightleftharpoons O^- + O_2$	3.6×10^{18}
7	$O + O + e^- \rightleftharpoons O^- + O$	3.6×10^{18}
8	$O_2 + O_2 + e^- \rightleftharpoons O_2^- + O_2$	3.6×10^{16}
9	$O + O_2 + e^- \rightleftharpoons O_2^- + O$	3.6×10^{16}
10	$O_2^+ + O^- \rightleftharpoons O_2 + O$	$3.6 \times 10^{19} T^{-1}$
11	$O + O^- \rightleftharpoons O_2 + e^-$	8.4×10^{13}
12	$O + O_2^- \rightleftharpoons O_2 + O^-$	4.8×10^{13}
13	$O_2 + O_2^- \rightleftharpoons O_2 + O_2 + e^-$	$5.4 \times 10^9 T^{1.5} \exp(9{,}913/T)$

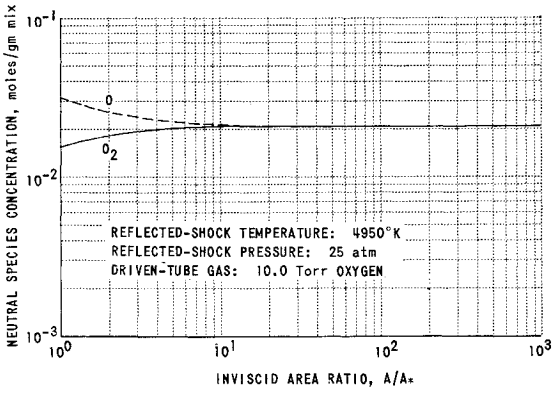

Fig. 1a Neutral species distribution in nozzle flow.

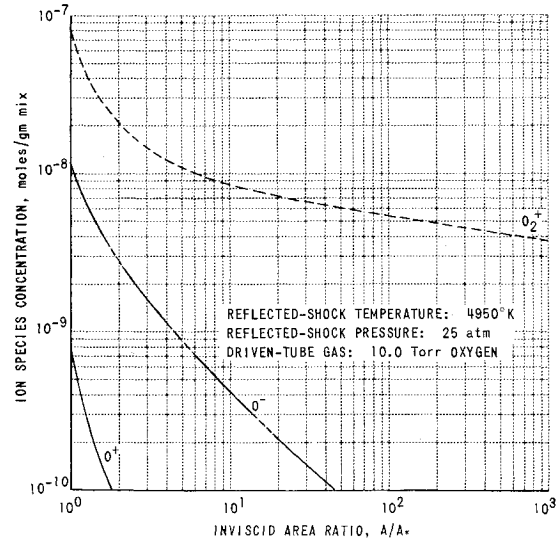

Fig. 1b Ion-species distribution in nozzle flow.

The variation of the neutral- and ion-species concentrations along the nozzle was calculated with this model, assuming the rate coefficient of reaction 4 to be $8.0 \times 10^{21}\ T_e^{-1.5}$, and is shown in Figs. 1a and 1b. The results for the neutral species concentrations indicate that the O_2 and O concentrations become frozen very early in the expansion because the three-body recombination reactions become unimportant. Therefore, variations in the rate coefficients for reactions 1 and 2 have very little influence on the rate coefficient deduced for reaction 4. The ion distributions shown in Fig. 1b indicate that O_2^+ was the dominant ion, by at least a factor of 100, at all of the measuring stations.

For the nozzle-flow calculations performed here the prescribed nozzle cross-sectional area was that of the inviscid core. The boundary-layer displacement thickness was computed using the method of Ref. 21. For the conditions of these experiments, the boundary-layer correction was small.

4. Determination of Rate Coefficient

The electron temperatures measured in the expanding oxygen plasma are presented in Fig. 2 and are compared with the calculated heavy-particle translational temperature. These measurements were performed with thin-wire probes located at 12.5, 22.5 and 32.5 in. ($A/A_* = 80$, 255, and 530) from the nozzle throat. The electron temperature measurements scatter approximately $\pm 10\%$ about an average linearly decreasing value which is typical of the results obtained in our previous work.[1,2]

Figure 3 presents a comparison of the electron-density measurements performed with the Langmuir probes and the microwave interferometers as a function of inviscid area ratio. As expected,[1] the Langmuir probe measurements at the 12.5-in. location fell well below the microwave-interferometer data while those at the 22.5-in. location were only slightly below. The probe data were interpreted using the free-molecular flow theory of Laframboise.[22] However, at these measuring stations the ion-neutral and neutral-neutral mean free paths were such that the flow was not free molecular with respect to the probe diameter, so that these probe data are not used in determining the reaction-rate coefficient. No attempt was made to apply a correction for collisional effects. An illustration of how this can be done, using the correction of Talbot and Chou,[23] is given in Ref. 24 for a nitrogen plasma. At the 32.5-in. station, where the flow is free-molecular, the two diagnostic techniques give consistent results.

Since the electron mean free paths are much greater than the probe diameter for the plasma conditions of interest here, the electron temperature measurements were not influenced by collisional effects. Results are presented in Ref. 24 that illustrate the insensitivity of the measured electron temperature to collisions in a nitrogen plasma. The electron temperature measurements performed at the 12.5 and 22.5-in. locations were necessarily used in the rate-coefficient determination.

The dissociative recombination reaction-rate coefficient was determined by matching the measured electron densities with the calculated results. Lines A, B, and C on Fig. 3 were calculated with the rate coefficient of reaction 4 (Table 1) given by $(8.0 \pm 2) \times 10^{21}\ T_e^{-1.5}$. These values of the rate coefficient bracket all of the experimental data with the exception of three data points at $A/A_* = 230$, which fall just outside of the predicted distributions. Line D was obtained using a rate coefficient value of $1.0 \times 10^{22}\ T^{-1.5}$ and the heavy-particle translational-temperature distribution instead of the measured electron-temperature distribution. The influence of the temperature history on the predicted electron-density distribution is evident.

Hansen[25] has previously argued that at elevated temperatures the temperature dependence of the rate coefficient for the reaction $NO^+ + e^- \rightleftharpoons N + O$ is given by $T^{-1.5}$. He assumed a constant transition probability at the N + O, NO^+ potential crossing in order to obtain the ionization rate via this mechanism. Then, relating the recombination rate coefficient to the ionization rate coefficient through the equilibrium constant, he found the recombination rate coefficient to be proportional to $T^{-1/2}[1 - \exp(\theta_v/T)]$ where θ_v is the characteristic vibrational temperature of NO^+. This same argument was applied here in order to obtain the temperature dependence of the rate coefficient used for the reaction $O_2^+ + e^- \rightleftharpoons O + O$.

The reaction-rate coefficient determined in this paper for the deionization of O_2^+ by the mechanism $O_2^+ + e^- \rightarrow O + O$ is

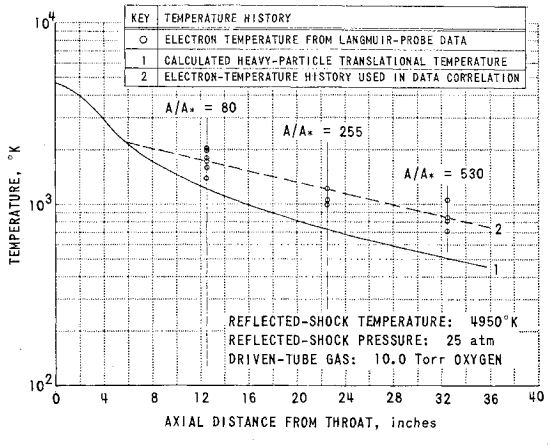

Fig. 2 Measured electron temperature in expanding oxygen plasma.

compared with those of previous investigators‡ in Fig. 4. Sayers[3] and Sayers and Kerr[4] each previously reported a high-temperature data point. Our value is approximately 2.3 times greater than the values reported by these authors.

The rate-coefficient data reported here are applicable to the temperature range 4950°K to 1800°K. The temperature dependence of the rate coefficient can be seen from the aforementioned relation to be $T^{-0.5}$ at low temperatures. The sensitivity of the predicted electron-density distribution to the electron-temperature dependence was investigated by using a $T^{-1.5}$ dependence in the range 4950°K to 2650°K, then switching to a $T^{-0.5}$ dependence for temperatures less than 2650°K. The influence of temperature dependence on the calculated electron-density at the last measuring station was an increase of approximately 10% over those shown by line B. This influence is smaller than the data scatter, and thus it is not possible to assess the rate-coefficient temperature dependence at low temperatures from the experimental data presented here. However, extrapolating the experimental data using a $T^{-0.5}$ temperature dependence from 2650°K to 300°K indicates good agreement with previously published experimental data as shown by the dashed line on Fig. 4.

5. Conclusions

The $O_2^+ + e^-$ dissociative-recombination rate coefficient was measured in an oxygen plasma that had expanded from an equilibrium reservoir condition of 4950°K and 25 atm pressure. The resulting rate coefficient is given by $k_r = (8.0 \pm 2) \times 10^{21}\ T_e^{-1.5}$ cm³/mole sec for an electron temperature range of approximately 4950°K to 1800°K.

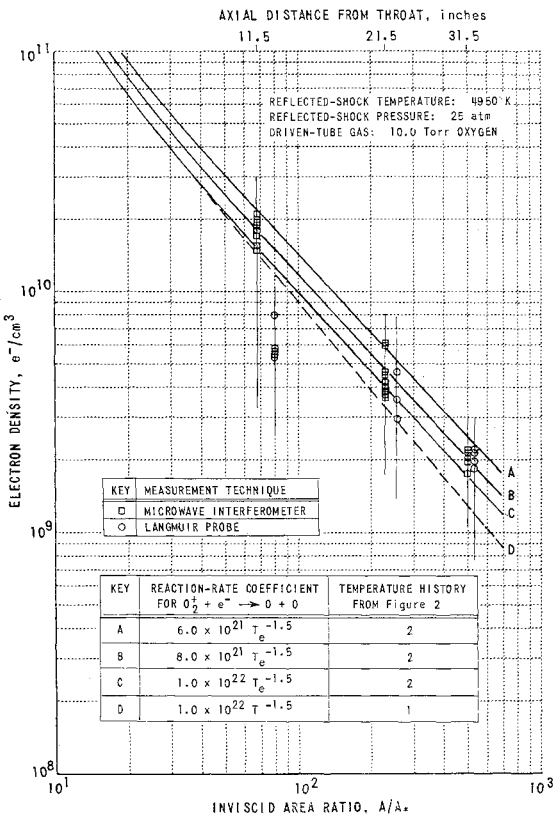

Fig. 3 Measured electron density in expanding oxygen plasma.

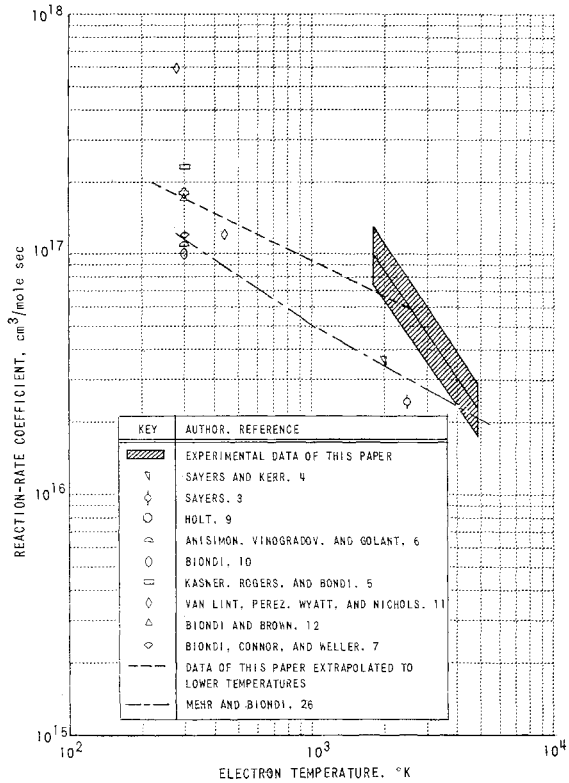

Fig. 4 Reaction-rate coefficient data for the reaction $O_2^+ + e^- \rightarrow O + O$.

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