New Concepts of the Chemistry of Electric-Discharge Oxygen-Iodine Lasers

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ABSTRACT

The chemistry of electric discharge driven oxygen iodine lasers (EOIL) has long been believed to have $O_2(a^1Δ_g)$ as the sole energy carrier for excitation of the lasing state $I(2P_{1/2})$, and $O(3P)$ as the primary quencher of this state. In many sets of experimental measurements over a wide range of conditions, we have observed persistent evidence to the contrary. In this paper, we review our experimental data base in both room-temperature discharge-flow measurements and EOIL reactor results, in comparison to model predictions and kinetics analysis, to identify the missing production and loss terms in the EOIL reaction mechanism. The analysis points to a significantly higher level of understanding of this energetic chemical system, which can support advanced concepts in power scaling investigations.

Keywords: Oxygen Iodine laser, kinetics, singlet molecular oxygen, beam quality

1. INTRODUCTION

The electric oxygen iodine laser (EOIL) holds considerable promise for a high power gas phase laser with excellent beam quality and good electrical efficiency. We have been using a high power microwave discharge, supersonic flow facility to study the kinetics, small signal gain, and laser output in order to understand the scaling properties of this system. A scaled system has the potential to be a much more compact and lighter-weight alternative to the well known chemical oxygen iodine laser (COIL), developed in 19771 and subsequently scaled to MW levels.2 In both EOIL and COIL, electronically excited metastable singlet oxygen, $O_2(a^1Δ_g)$ [hereafter also referred to as $O_2(a)$], collisionally pumps iodine atoms to produce single-line laser output on the $I(2P_{1/2}→2P_{3/2})$ transition at 1.315 µm. EOIL offers all the advantages of COIL such as excellent beam quality,3 good propagation properties,2 and high power operation. Moreover, EOIL eliminates the complex, massive and hazardous liquid-based chemistry system that is required in COIL to produce singlet molecular oxygen to power the laser. At present, EOIL technology test facilities are operated as open-cycle systems. However, due to its all-gas-phase feedstock, the device is well suited for closed-cycle operation.

Our technical approach is based on several years of research and development on the chemical kinetics and performance of the electric oxygen iodine laser system.4-17 The electric discharge methods employed (high power microwave, radio frequency, and pulser-sustainer) typically operate on mixtures of $O_2$ and helium and produce several energetic species. Most of these species are short-lived after the gas exits the active discharge. O atoms and $O_2(a)$ are the primary energetic species that survive into the reaction zone, where $I_2$ is introduced into the flow stream. In EOIL test systems to date, flowing He/$O_2$ mixtures are passed through an electric discharge to produce the $O_2(a)$ and atomic oxygen, NO is introduced to reduce the O concentration, $I_2$ vapor is added to the subsonic active-oxygen flow just upstream of a supersonic nozzle, and power is extracted from the low-temperature supersonic flow. In a recent effort, Carroll and coworkers have scaled an rf-discharge driven EOIL system to laser powers in excess of 100 W.16,17

The conventionally accepted mechanism for the reactions between $I_2$ and the effluent of the oxygen discharge is8,9,13

\[
\begin{align*}
O + I_2 & \rightarrow IO + I \\
O + IO & \rightarrow O_2 + I \\
O_2(a) + I & \rightarrow O_2(X) + I^* \\
O + I^* & \rightarrow O + I \\
I^* & \rightarrow I + hv
\end{align*}
\]

(1)

$I^*$ excitation (near-resonant, reversible)
$I^*$ quenching
Lasing

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Atomic oxygen provides rapid dissociation of I₂, so that no O₂(a) is used in the dissociation step. However, atomic oxygen in large concentrations is also a significant quencher of the laser emission, so its concentration must be actively controlled. This is done by addition of NO₂ or NO, using the coupled reactions

\[
\begin{align*}
O + NO + M & \rightarrow NO_2 + M \\
O + NO_2 & \rightarrow NO + O_2
\end{align*}
\] (2)

to reduce the O concentration (where M signifies a generic third-body collision partner, e.g. O₂ and He). Several papers have previously demonstrated that when optimum amounts of NO₂ or NO are introduced, the optical gain is greatly increased and is sufficient to support lasing.⁴⁻⁹,¹³,¹⁴

In the reaction scheme given above, when the I⁺⁺O quenching reaction rate is sufficiently reduced, the inversion ratio [I⁺⁺]/[I⁻] is controlled primarily by the reversible energy transfer reaction between O₂(a) and atomic iodine, Reaction (1). Thus in the absence of other loss terms, the optical gain is directly related to the O₂(a) yield (i.e. the fraction of the incoming oxygen that is excited to the O₂(a) state) through the equilibrium constant for Reaction (1). Since the energy of O₂(a) is slightly higher than that of I⁺⁺, this equilibrium shifts strongly towards I⁺⁺ excitation as the temperature is reduced. For this reason, test systems usually employ a supersonic nozzle to reduce the temperature of the reacting mixture to 100-200 K. For a supersonically cooled flow of ~150 K and no quenching loss of I⁺⁺, the idealized threshold for optical gain is a singlet oxygen yield of ~4.4%. Typical O₂(a) yields observed for our microwave discharge systems range from 10% to 25%, for dilute mixtures of O₂ in He in low-pressure, low-power (1 to 3 Torr, 100 W) and high-pressure, high-power (40 to 60 Torr, 1 kW) conditions. Thus the conventional EOIL reaction mechanism would indicate that it should be quite straightforward to achieve positive optical gain under these conditions.

In practice, this is not the case. In our experience, it is always necessary to add NO (or NO₂) in order to achieve positive gain. We invariably observe net absorption on the I⁺⁺-I⁻ transition if NOx is not added, even when the O₂(a) yield is far above the idealized threshold. From an empirical perspective, it is logical to presume that this effect is due to the quenching of I⁺⁺ by O as described above. However, quantitative modeling of the reaction rates using the measured species concentrations shows that this is not the correct view. The actual O-atom concentrations are considerably smaller than one might expect from models of the discharge kinetics, and the O + I⁺⁺ quenching rate coefficient is now known to be modest in magnitude.¹⁸ This conundrum is illustrated by the model-to-data comparison in Figure 1. The data points (with curvefits) are the results of measurements in the supersonic cavity PSI EOIL reactor¹³,¹⁴ described below, for the measured O₂(a) and O yields given in the figure. Without NO, the net gain is negative, signifying absorption; when sufficient NO is added to give the maximum gain, the gain is positive by a similar magnitude. The solid curves show the results of kinetics model calculations using the widely accepted conventional reaction mechanism and well-known rate coefficients¹³ together with the measured O₂(a) and O yields and density and temperature profiles.

The model fails on two very substantial counts. First, it fails to account for the pronounced net absorption when NO is not added. Second, it fails to account for the large increase in gain when NO is added. In short, the effect of O to quench I⁺⁺ is very small and does not account for the observed phenomenology by a large margin. This means that there are...
major missing ingredients in the model involving both I* quenching and I* excitation. We have addressed some aspects of these issues in previous work. In this paper, we review our experimental data base in both room-temperature discharge-flow measurements and EOIL reactor results, in comparison to model predictions and kinetics analysis, to identify the missing production and loss terms in the EOIL reaction mechanism. The analysis points to a significantly higher level of understanding of this energetic chemical system, which can support advanced concepts in power scaling investigations.

2. EXPERIMENTAL METHODS

To investigate EOIL kinetics, we have focused our experiments on conditions which isolate the primary reactions of interest, i.e. dilute O$_2$/He discharge mixtures, low reagent concentrations, and well-defined flow conditions. For fundamental investigations of discharge production, active-O$_2$ kinetics, and I* production and quenching, we have used a conventional room-temperature discharge-flow reactor shown in Figure 2. The 2450 MHz microwave discharge is maintained by an external-cavity, Evenson-style resonator at typically 70 to 100 W (E/N = 10-100 Td). Flow rates are 1-5 mmole/s at pressures of 1-10 Torr. The main flow reactor is a modular 5 cm i.d. Pyrex tube with fixed and movable inlets for reagents including I$_2$, NO and NO$_2$. Optical diagnostic measurements of the reactant and product species are made at a set of window ports at the downstream end of the reaction zone. Typical flow velocities in the main flow tube range from 500 to 2500 cm/s.

To examine the reaction kinetics for EOIL flow conditions, we have developed a bench-scale subsonic/supersonic EOIL flow reactor driven by a 1-5 kW coaxial microwave discharge (E/N = 10-50 Td). The apparatus is illustrated in Figure 3. The subsonic flow section transitions from the coaxial, 2.5 cm diameter discharge outlet to a rectangular flow duct 1 cm high by 5 cm width. Total flow rates are 40-100 mmole/s, resulting in subsonic pressures of 30-70 Torr and subsonic flow velocities near $10^4$ cm/s. The gas flow passes through a Mach ~2 nozzle immediately downstream of the I$_2$ inlet, into the supersonic flow cavity. Optical diagnostic measurements of the reactant and product species are made in both the subsonic and supersonic flow sections. The experiments discussed here were all performed with 1 kW discharge power. Gas temperatures are 330-350 K at the subsonic diagnostic port and 120-150 K in the supersonic cavity. Typical laser output powers are on the order of 100-150 mW using 1-inch diameter max-R mirrors on the supersonic cavity, with a measured beam quality $M^2 = 1.08 \pm 0.01$.

We use a suite of advanced optical emission and absorption diagnostics to monitor the absolute concentrations of all of the key reactant and product species: O$_2$(a), O, O$_3$, I$_2$, I, I*, and temperature. The details and calibration procedures are described elsewhere. The diagnostics are listed in Table 1.
Table 1. Diagnostics Used to Characterize the Discharge Laser Devices

<table>
<thead>
<tr>
<th>Species or Parameter</th>
<th>Method</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I^*$, $I$, $T$</td>
<td>TDL Absorption/Gain</td>
<td>1315 nm</td>
</tr>
<tr>
<td>$O_2$(a,b), $I^*$</td>
<td>InGaAs array emission spectrometer</td>
<td>700-1500 nm</td>
</tr>
<tr>
<td>$O$</td>
<td>NO-O chemiluminescence</td>
<td>580 nm</td>
</tr>
<tr>
<td>$I_2$ flow rate</td>
<td>LED micro-absorption</td>
<td>488 nm</td>
</tr>
<tr>
<td>Ozone</td>
<td>UV micro-absorption</td>
<td>254 nm</td>
</tr>
<tr>
<td>$I_2$ (B)</td>
<td>Visible emission spectrometer</td>
<td>500-700 nm</td>
</tr>
</tbody>
</table>

3. DISCHARGE PRODUCTION OF $O_2$(A), $O$

The production of $O_2$(a) and $O$ in electric discharges occurs through energetic electron impact on $O_2$. We have previously discussed the details of the discharge dynamics.\(^8\)\(^9\)\(^10\) For the conditions of our low-pressure discharges, e.g. (5-20)% $O_2$/He at 1.5-3 Torr and 70-100 W, E/N is 50-100 Td and the characteristic electron energies are 3-6 eV. Electron number densities are in the $10^{11}$-$10^{12}$ cm\(^{-3}\) range. Within the active discharge, $O_2$(a) loss terms by electron impact include superelastic quenching, dissociation, dissociative attachment (to form $O$), and ionization (to form $O_2^−$). In addition, $O_2$(a) can react with $O^-$ to form either $O_3$ or $O_2^-$; at the elevated temperature of an active discharge, the primary branch is the charge transfer to $O_2^-$\(^19\)\(^20\). We model the production and loss rates using electron-impact cross sections compiled by Phelps\(^21\) and the $O_2$ dissociation cross section determined by Cosby.\(^22\) Atomic oxygen has no significant loss terms on the time scale of the flow time through the discharge.

We observe the time-dependent production of $O_2$(a) and $O$ by varying the gas flow rate and flow velocity at constant pressure and discharge conditions. This provides measurements of species concentrations as functions of residence time within the active (light-emitting region) discharge. Since the measurements are made at a fixed location well downstream of the discharge exit, we must consider possible losses between the discharge exit and the measurement point. This would occur primarily by quenching of $O_2$(a) and recombination of $O$ on the glass reactor surfaces. Repeated determinations of the relative $O$ and $O_2$(a) concentrations along the length of the flow tube show no significant losses within the main flow reactor for the flow and pressure conditions of the discharge production measurements.

All of our measurements consistently show $[O_2$(a$)] \geq [O]$, in marked contrast to model predictions which show $[O] > [O_2$(a$)]$. Example comparisons of data to model predictions are shown in Figure 4. In Figure 4a, the computed $O_2$(a) production agrees well with the data, however the computed $O$ production is more than an order of magnitude larger than observed. In Figure 4b, we include diffusion-limited loss of $O$ by collisions with the hot walls within the active discharge, and the computed $O$ profile comes closer to the data. It may be that the $O_2$ dissociation cross section used in the calculations is too large, however we suspect that there may be considerable $O$ loss on the hot glass surfaces immediately downstream of the discharge exit and prior to entry into the main flow reactor.

![Figure 4. Comparisons of observed and computed $O_2$(a) and $O$ production in the low-pressure microwave discharge. (a) no wall loss of $O$; (b) with wall loss of $O$](image-url)
The main point is that a fairly straightforward model of the discharge greatly overpredicts the actual, measured O concentrations reaching the reaction zone. We have observed similar results in our EOIL flow reactor; as noted in results shown below, we typically observe O yields in the subsonic flow which are less than half of the O$_2$(a) yields, despite discharge predictions to the contrary. For this reason, we use actual measured O and O$_2$(a) yields as the starting boundary conditions for modeling the EOIL chemistry, rather than model-computed discharge production.

4. $I^*$ QUENCHING AND EXCITATION

In previous work, we observed quantitative $I^*$ and I production in the discharge-flow reactor for the reaction of I$_2$ with known concentrations of O and O$_2$(a). The quenching of $I^*$ resulted in loss of O$_2$(a) at a rate of \(~100 \text{ s}^{-1}\). Through an analytical model of the $I^*$ production and loss kinetics, we related this O$_2$(a) loss rate to the $I^*$ quenching rate and determined a first-order $I^*$ quenching rate of \(~5000 \text{ s}^{-1}\). This loss is consistent with the quenching reaction

$$I^* + O_2 \rightarrow I + O_2(X, v \leq 5), k = 3 \times 10^{-12} \text{ cm}^3/\text{s}$$  \hspace{1cm} (3)

We note that O$_2$(X, v \leq 5) is nearly resonant with $I^*$ and is thus the highest vibrational level of O$_2$(X) that can be formed by the energy transfer. Incorporation of this reaction into the kinetics model accounts for the net I-$I^*$ absorption observed when no NO$_2$ is added, and for the small positive gain observed when the O is almost completely removed by NO$_2$. Here we extend that analysis to the EOIL supersonic flow case.

A representative sample of EOIL data from our lab is shown in Figure 5, as plots of measured quantities vs. added NO flow rates. The experiments used a discharge mixture of 5% O$_2$/He + NO at 47 mmole/s and 1 kW discharge power. Unreacted O$_2$(a) and O yields were determined in the subsonic flow upstream of the I$_2$ inlet, and the gain and $I^*$ measurements were made in the supersonic flow. As shown in Figure 5a, the gain is negative (net absorption) for zero NO, even though the initial O$_2$(a) yield is ~20%, far in excess of the threshold for gain in the supersonic flow (~4%). With the addition of NO, the gain becomes positive and passes through a broad maximum near an NO flow rate of ~0.5 mmole/s. However, as shown in Figure 5b, the inversion ratio $[I^*]/[I]$ continues to increase with increasing NO, even though the gain decreases past its maximum.

![Figure 5. Effect of NO on gain, yields, and inversion ratio: 4.35 cm downstream of nozzle throat, 5% O$_2$/He at 47 mmole/s, 4.6 \( \mu \)mole/s I$_2$, 1 kW discharge power. (a) Supersonic gain, subsonic O$_2$(a) and O yields prior to I$_2$ injection; (b) supersonic $I^*$, I, $I^*/I$](image)

At NO levels beyond the optimum titration point, the O-atom concentration is reduced relative to [I$_2$] to the degree that the O-atom reactions are too slow to fully dissociate the I$_2$, resulting in diminishing I-atom concentrations. The gain decreases because the total I-atom concentration, $[I^*] + [I]$, decreases. It appears from these data that the continuing increase in the inversion ratio is due not to removal of O-atoms (which are already removed), but rather to an $I^*$ excitation process triggered by the presence of NO and/or NO$_2$. Furthermore, it appears that implementation of a secondary electric discharge to promote dissociation of I$_2$ in the absence of O, i.e. at high NO, would greatly enhance the
gain that can be achieved. Based on the observed inversion ratios, if the total I-atom concentration observed at zero NO (no O removal) could be maintained by electric dissociation of I₂, then the gain at the highest NO flow would be more than tripled.

To model the reaction kinetics in the subsonic and supersonic flows, we use the widely accepted conventional EOIL reaction set discussed elsewhere. The pressure and temperature profiles are taken from the on-axis values computed by the FLUENT CFD code and confirmed by measurements of pressure, O₂(a) number densities and rotational temperatures, and I-atom translational temperatures. Initial species concentrations are determined from the measured input flow rates and pressures, and the measured initial (unreacted) O₂(a) and O yields. For the dilute mixtures and low species concentrations in our experiments, the predicted reaction outcomes are sensitive only to the limited set of basic reactions discussed in Section 1. The model calculations begin with the initial conditions and measured species concentrations at the discharge exit, and proceed down the subsonic flow and through the supersonic expansion, computing the evolution of all species concentrations with flow time. Here we focus on comparisons of predicted and observed optical gains in the supersonic flow with and without addition of NO to optimize the gain. The experimental data used in the comparison are not at all unique, and are quite representative of a substantial data base over a wide range of flow conditions and O₂ mole fractions.

The failures of the conventional reaction set are illustrated in Figure 1: the model fails to account for the “negative gain” observed without NO, and for the magnitude of the increase in gain observed when NO is added. Figure 6 illustrates the analysis of the loss process in the absence of NO. We introduced the single reaction (3) to account for additional quenching of I*, and varied the assumed rate coefficient (with no temperature dependence) to fit the “negative gain” data. The fit is very good for k₃ = 4 x 10⁻¹² cm³/s, and is neatly bracketed by the calculated curves for 3 x 10⁻¹² and 5 x 10⁻¹² cm³/s. This is remarkably consistent with our room-temperature discharge-flow reactor results at much lower pressures, species concentrations, and flow velocities.

Figure 6. Comparison of computed and observed “negative gain” profiles in supersonic flow for the conditions given in Figure 1, no NO added. Gain data for the case with added NO are also shown. The computed curves are for different values of the rate coefficient for I* quenching by O₂: I* + O₂ → I + O₂, as indicated in the legend.

Figure 7 shows the analysis for the recovery of I* excitation when NO is added, with quenching by Reaction (3) included as above. When the only effect of NO in the model is to remove O-atoms by reactions with NO and NO₂, the predicted gain is negative and only slightly larger than the case without NO. As we surmised by inspection of the [I*]/[I] data in Figure 5, it appears that there must be an additional path to I* excitation that is initiated by the NOx chemistry.

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Our investigation of this question is still incomplete, however we discuss here some preliminary concepts. The additional I* excitation rate required to offset the loss rate must be rather large. This implies relatively large precursor species concentrations if the rate coefficients are not unusually large. Judging from the computed and observed species concentrations in the subsonic and supersonic flows, there are very few species which could have sufficient concentration and energy to drive this excitation rate. One of the most likely precursors, which would be “dark” to our optical sensors, is vibrationally excited ground-state \( \text{O}_2(\text{X}, \nu) \). If higher vibrational states are populated, they can potentially excite I* by direct energy transfer to I:

\[
\text{O}_2(\text{X}, \nu) + \text{I} \rightarrow \text{O}_2(\text{X}, \nu - \nu') + \text{I}^*
\]

As noted above, \( \text{O}_2(\text{X}, \nu) \) produced in the discharge is expected to be rapidly quenched prior to the reaction zone, primarily by collisions with \( \text{O} \) and with the reactor walls. However, there are a number of reactions involving NOx species and active-oxygen species that are sufficiently exoergic to produce \( \text{O}_2(\text{X}, \nu) \). Examples are:

\[
\begin{align*}
\text{O} + \text{NO} + \text{M} & \rightarrow \text{NO}_2^*(3.2 \text{ eV}) + \text{M} \\
\text{O} + \text{NO}_2 & \rightarrow \text{NO} + \text{O}_2^* + 2 \text{ eV} \\
\text{O} + \text{NO}_2 + \text{M} & \rightarrow \text{NO}_3^*(2.2 \text{ eV}) + \text{M} \\
\text{O} + \text{NO}_3 & \rightarrow \text{NO}_2 + \text{O}_2^* + 3 \text{ eV} \\
\text{NO} + \text{O}_3(\nu \geq 1) & \rightarrow \text{NO}_2 + \text{O}_2^* + 1.9 \text{ eV}
\end{align*}
\]

These reactions have the capacity to introduce significant vibrational energy content into the active-oxygen mixture, perhaps enough for multiple I\( \rightarrow \text{I}^* \) transfers for a single excited precursor molecule. The concept of \( \text{O}_2(\text{X}, \nu) \) as an energy carrier for \( \text{I}^* \) excitation emerges from catalytic EOIL experiments is described in a companion paper at this symposium.\textsuperscript{23} We are proceeding to analyze this system with a more critical and comprehensive approach. Clearly in such a model it is important to track the detailed, level-by-level vibrational excitation and deactivation kinetics, however this is poorly known for the active-oxygen-NOx reaction system.
5. CONCLUSIONS

We have developed an extensive kinetics data base on the excitation of I* by discharge-generated active-oxygen. This data base exposes major, previously unknown chemical processes in what we previously considered to be a straightforward, well-understood reaction mechanism. The data base comes from two very different discharge-flow reactors, one a conventional low-pressure, low-power microwave discharge-flow tube at room temperature, and the other a high-pressure, medium-power, microwave-driven subsonic/ supersonic EOIL laser device. The data from these two reactors spans an order of magnitude in pressure, flow velocity, and species concentrations, and ranges in temperature from near 300 K to below 150 K. The key element of these measurements is the use of a comprehensive optical diagnostic suite to determine accurate concentrations of all of the known reactants and products. This imposes a strong constraint on model simulations of the chemistry: for the widely accepted “conventional” chemistry model, there are no adjustable parameters that can be used to rationalize the experimental and computed results. In comparisons between the model predictions and a set of representative EOIL gain data, we see that the “conventional” mechanism fails on two very important counts. First, the model fails to account for the pronounced I* loss and “negative gain” that we observe when NO is not added to optimize the gain. This discrepancy is resolved by including the quenching of I* by O2 with a rate coefficient in excellent agreement with conclusions reached earlier from the low-pressure flow reactor data. Second, the model fails to account for the large increase in gain achieved when NO is added to the reacting flow. The EOIL data indicate that the addition of NO triggers energetic reactions between NOx species and active-oxygen species which produce an energy carrier that excites I*. This energy carrier is most likely vibrationally excited O2(X,v). Atomic oxygen, which was previously considered to be primarily responsible for the I* quenching and NO effects, plays a relatively minor role in our experiments. We are continuing to refine this preliminary analysis to substantiate the role of O2(X,v) in the EOIL reaction mechanism.

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