NEGATIVE ION DETACHMENT

A. Mandl

Avco Everett Research Laboratory

Prepared for:

Office of Naval Research
Advanced Research Projects Agency

30 June 1972

DISTRIBUTED BY:

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151
SUMMARY TECHNICAL REPORT
(1 June 1971 - 30 June 1972)

CONTRACT NO. 00014-71-C-0386

NEGATIVE ION DETACHMENT

***************

ARPA ORDER NO. 1479
PROJECT CODE 421

PRINCIPAL INVESTIGATOR:

Dr. A. Mandl
Avco Everett Research Laboratory
Everett, Massachusetts 02149
Telephone - A/C 617, 389-3000, Extension 648

SCIENTIFIC OFFICER:

Director, Physics Program
Division of Physical Sciences
Office of Naval Research
800 North Quincy Street
Arlington, Virginia  22217

EFFECTIVE DATE OF CONTRACT: 1 June 1971

CONTRACT EXPIRATION DATE: 30 June 1973

AMOUNT OF CONTRACT: $108,913
RESULTS

We have measured several associative detachment rates of F⁻ negative ions by various gases. These reactions studied are listed below.

\[
\begin{align*}
    F^- + F & \rightarrow F_2 + e - 1.9 \text{ eV} \quad (1) \\
    F^- + O_2 & \rightarrow O_2 + e - 2.8 \text{ eV} \quad (2) \\
    F^- + O & \rightarrow OF + e - 0.5 \text{ eV} \quad (3) \\
    F^- + CF_2 & \rightarrow CF_3 + e + 0.5 \text{ eV} \quad (4)
\end{align*}
\]

Measurements on Reactions (1) and (2) had been started under the previous contract and were finished during the first part of this contract. Figures (1) and (2) show our measured rate constants and our fits to the data. All the rate constants which we have measured to date (including the previous work) are listed in Table I.

Our major aim under this contract was to measure Reaction (3), i.e. associative detachment of F⁻ by atomic oxygen. The source of atomic oxygen in these measurements is ozone (O₃) which breaks up under the conditions of our shock tube into equal mole fractions of O and O₂ so that we see simultaneous detachment by both O and O₂. Thus, the rate of detachment by O₂ had to be measured (previous contract)
MEASURE COLLISIONAL DETACHMENT RATE
OF $F^-$ BY $F$

$$F + F^- \rightarrow k \rightarrow F_2 + e^{-} - 1.9\text{eV}$$

$$k = 1.4 \times 10^{-10} \text{ e}^{-22,000/\text{m}}$$

Fig 1
\[ k(O_2) = 2.5 \times 10^9 e^{-27,600/} \]

Fig. 2.
<table>
<thead>
<tr>
<th>REACTION</th>
<th>( k \ (\text{cm}^3/\text{sec}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{F}^{-} + \text{Ar} \rightarrow \text{F} + \text{e} + \text{Ar} )</td>
<td>( 1.2 \times 10^{-11} \ e^{-40,000/T} )</td>
</tr>
<tr>
<td>( \text{F}^{-} + \text{Cs}^{+} \rightarrow \text{F} + \text{e} + \text{Cs}^{+} )</td>
<td>( 2.8 \times 10^{-9} \ e^{-40,000/T} )</td>
</tr>
<tr>
<td>( \text{F}^{-} + \text{N}_2 \rightarrow \text{F} + \text{e} + \text{N}_2 )</td>
<td>( 6.0 \times 10^{-11} \ e^{-40,000/T} )</td>
</tr>
<tr>
<td>( \text{F}^{-} + \text{CO} \rightarrow \text{F} + \text{e} + \text{CO} )</td>
<td>( 1.7 \times 10^{-10} \ e^{-40,000/T} )</td>
</tr>
<tr>
<td>( \text{F}^{-} + \text{H}_2 \rightarrow \text{HF} + \text{H}^{-} )</td>
<td>( 2.8 \times 10^{-11} \ e^{-9,400/T} )</td>
</tr>
<tr>
<td>( \text{F}^{-} + \text{F} \rightarrow \text{F}_2 + \text{e} )</td>
<td>( 1.4 \times 10^{-10} \ e^{-22,000/T} )</td>
</tr>
<tr>
<td>( \text{F}^{-} + \text{O}_2 \rightarrow \text{O}_2 \text{F} + \text{e} )</td>
<td>( 2.5 \times 10^{-9} \ e^{-27,600/T} )</td>
</tr>
<tr>
<td>( \text{F}^{-} + \text{O} \rightarrow \text{OF} + \text{e} )</td>
<td>( 2.0 \times 10^{-10} \ e^{-14,600/T} )</td>
</tr>
<tr>
<td>( \text{F}^{-} + \text{CF}_2 \rightarrow \text{CF}_3 + \text{e} )</td>
<td>( \sim 10^{-12} )</td>
</tr>
</tbody>
</table>
and subtracted from these data. Our measured rates of detachment of $F^-$ by $O$ and $O_2$ are given in Fig. 3. Note that at the high temperature end ($T \sim 5000^\circ K$) the $O$ and $O_2$ detachment rates become comparable but in the region of interest for boundary layer conditions, i.e. $T \sim 2800^\circ K$, the atomic oxygen detachment rate dominates. We will discuss the significance of this below.

As I had mentioned in one of the quarterly management reports, there were two milestone experiments which we had to perform initially in order to insure that we would be able to, in fact, use ozone in our system. First, we had to insure that our shock tube could hold ozone for reasonable periods of time without significant decomposition to $O_2$. In order to assure this, the tube had to be passivated. Passivation is a process in which the stainless steel walls of the shock tube are allowed to be oxidized by the highly active ozone until sufficient oxides build up on the surface making it non-reactive to ozone.

In order to show this passivation, we did the following experiment: A one meter cell for measuring ozone concentrations was attached to our shock tube. The one meter cell had a stainless steel seal which was not yet exposed to ozone and therefore not passivated. There is a valve separating the shock tube from the cell. The shock tube was filled with a mixture of ozone and argon gas. Periodically (about once an hour) the one meter cell was filled with the ozone mixture from the shock tube and the valve then closed. We then monitored the ozone in the one meter cell. The first measurement, immediately after the cell is filled, tells us essentially what the
$k(0) = 2 \times 10^{10} \exp(-14,600 \text{ cm} / \text{mV})$

Fig 3

**Note:** Data points go with $F^- + O$ curve.
concentration of ozone is in the shock tube, since not much decay has yet occurred in the cell. The ozone density measurements after this, however, gives us the rate of ozone decay in the cell. The cell is pumped out after this decay is observed, and after one hour the process is repeated. Thus, the first measured point in each case gives us the decay rate of ozone in the shock tube. Figure 4 shows data obtained in the above manner after passivating the shock tube. Note that during the course of these measurements we see that the decay rate in the one meter cell is slowing, i.e. the cell is being passivated.

The second milestone experiment was to measure the effect of particulates (.07μ CsF particles in our case) on ozone decomposition. We observed that over the time scale of our experiment, i.e. ~ 60 seconds, no significant ozone decomposition was seen. Measurements of this type are, of course, of great significance for upper atmospheric physics. To my knowledge, these are the first laboratory measurements of the survival of ozone in gas containing a known quantity of particulates.

With the knowledge that ozone would not significantly decay when mixed with CsF particles in our passivated shock tube, we were able to proceed with our measurements. These results are summarized in Fig. 3.

Finally, we have made some measurements of $F^-$ detachment by $\text{CF}_2$. The $\text{CF}_2$ is produced by the decomposition of $\text{C}_2\text{F}_4$ (a very rapid process) at the shock front. We have not fully analyzed this data yet but it does give a rate of roughly $10^{-12} \text{ cm}^3/\text{sec}$. This rate should not have a large temperature dependence since the reaction $\text{CF}_2 + F^- \rightarrow \text{CF}_3 + e$ is exothermic.
PASSIVATION OF METZ CELL

OZONE DECAY IN SHOCK TUBE

OZONE DECAY IN METZ CELL

Fig 4
SIGNIFICANCE OF MEASUREMENTS

The original purpose of this program was to supply $F^-$ collisional detachment rates for the 14 species limited-partial-equilibrium model developed at AERL for the Teflon boundary layer. A major assumption of this model was that all the $F^-$ was detached in the boundary layer, i.e. all electrons were free. However, there were no kinetics data to support this assumption. As we measured our detachment rates of $F^-$, it became clear that none of our measurements for species like $N_2$, $O_2$, etc., present in the boundary layer gave rates fast enough to detach $F^-$. Thus, the validity of one of the main assumptions of the 14 species limited partial equilibrium model became questionable.

Figure 5 gives the minimum detachment rate (solid lines) necessary for different species at various altitudes to produce detachment by $F^-$ in boundary layer flow times. The dashed lines are our measured detachment rates. It is clear that our measured detachment rates for $N_2$, $CO$, $F$, and $O_2$ detachment are too low. We had suggested, therefore, that because of its possibly low activation energy, the rate of detachment of $F^-$ by atomic oxygen might be fast enough to cause $F^-$ detachment in the boundary layer. The measurements obtained for atomic O show that $F^-$ detachment by atomic oxygen is fast enough to give complete detachment in the boundary layer of a Teflon vehicle and tends to support the AERL model.

If it had turned out that detachment by O was not fast enough to give full $F^-$ detachment in the boundary layer, then the 14 species model would have had to be significantly revised and possible detachment
Fig. 5 Minimum Rate Constants for Electron Detachment. Solid lines give minimum values of the rate constant necessary for complete detachment of $F^*$ in the boundary layer of a Teflon ablating vehicle at various altitudes. The density, $n$, used is the maximum value of density, $n_{max}$, in the region of the boundary layer above 2500$^\circ$K as given by the AERL model in which 14 species are in equilibrium. The dashed curves are our measured values of rate constants. Complete detachment will occur below the intersection of a dashed and solid curve of the same species.
by CF₂ would have had to be considered. In that case detachment by CF₂ would have been quite important, and we had planned to measure this rate as part of this program. In any case we have measured the CF₂ detachment rate, although the significance of this rate to the overall program is now of lesser importance.
PUBLICATIONS


TALKS