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004 EPA STAR Graduate Fellowship Conference *Next Generation Scientists—Next Opportunities*

hlorine Atom Reaction Kinetics Under Lower Stratospheric and Upper Tropospheric Conditions

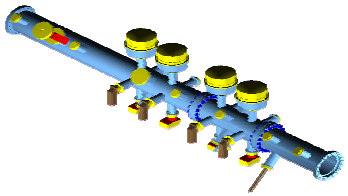
bstract

e reaction kinetics of many critical atmospheric reactions ain poorly understood under relevant atmospheric peratures and pressures. Of particular importance are ctions involving chlorine atoms, which play a crucial role in y catalytic loss cycles. The uncertainty in this data limits the uracy of models to forecast the trends of key atmospheric cies. This work plans to study key chlorine atom reaction etics, including:

$Cl + CH_4 \rightarrow CH_3 + HCl$ (1)
$ClOO + NO + M \rightarrow O_2 + ClNO + M$ (2)

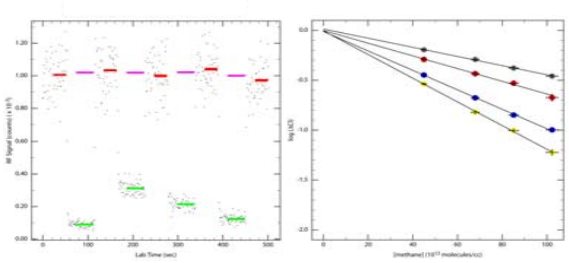
h of these reactions represent a sink for Cl atoms. Reaction as been studied extensively, but not at low T. Reaction 2 has y recently been identified as a potential loss process, and uires further study at low temperature due to its thermal ability.

xperimental



diameter makes the system essentially wall-less.
our separate resonance fluorescence (RF) axes detect Cl ms in the reaction zone.
l atoms are produced via microwave discharge.
ow temperatures are achieved by the simultaneous ogenic cooling of the walls and the carrier gas.
xcess reagent is injected upstream via loop injector to sure complete mixing.

Results



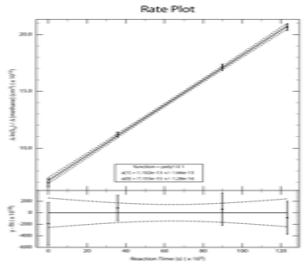


Figure 3. The decays from figure 2 are plotted versus their corresponding axis, yielding the rate constant. Since the velocity of the flow is known, the inter-axis spacing can be converted to time. Reaction time is defined as 0 at the first axis: the x-intercept indicates where the radical and reagent first mix. The lower panel shows the fit residuals with a 95% confidence interval.

Future Experimental Work

*System is primed for cold temperature data.

*Modify RF axis to increase signal: this is of particular importance when introducing oxygen to the system due to it's absorption in the same region as Cl.

Impact

.Chlorine Kinetics

* This work will elucidate key reactions in the upper atmosphere and improve the accuracy of models that are used to predict future global trends in ozone loss and other key public health issues.

.Future Possibilities

* Only a few minor modifications are needed to allow the system to measure other key radicals: the work here paves the way for a vast array of future studies involving a large variety of crucial atmospheric species.

Acknowledgments

I would like to thank Professor James Anderson and his research group for their valuable input and assistance with all phases of this work. I would also like to acknowledge the EPA STAR Fellowship Program for their generous financial support.

References

1. Sander, S. P et al. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*; Jet Propulsion Laboratory Publication No. 02-25, 2003

This fellow is sponsored by EPA's STAR or Greater Research Opportunities (GRO) Program.