Technical Progress Report

Kinetics and Mechanisms of Key Elementary Processes of Importance to High Temperature Combustion Chemistry

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I. Summary of Activities, 12-16-85 through 12-31-86

We continued to support the graduate student assigned to the project during the initial budget year. She has now completed her experimental work on the NRL shock tube facility and is engaged in final data analysis and modeling. She is expected to complete all requirements for the PhD by May 1987.

A postdoctoral research associate was added to the project staff during the period. He has been trained in the operation of the shock tube facility and has now been designated as the primary operator of the system.

A second postdoctoral associate received partial support from the contract for the purpose of setting up and testing a photon-counting system at CUA. This apparatus is being used in conjunction with a heated reactor to determine reaction rates by the detection of chemiluminescence from excited products.

The second graduate student, who received partial support from the contract during this reporting period, has completed the construction of the stirred-flow reactor system at CUA. He has calibrated the gas-chromatographic analysis system for stable products and has begun to study reactions of CH_3O at intermediate temperatures.

The shock tube data acquisition system developed by one of the principal investigators (WAS) was fully tested and implemented during the period. Several new features have been added to facilitate the data analysis and increase the speed of the system.

RRKM and kinetic modeling programs have been converted from the DEC-10 to the newly-installed large-scale VAX computer system at CUA, thereby achieving significant improvements in our computational capabilities.

Publication activity resulting from work supported by the contract during this reporting period consists of two papers published, a third accepted, and a fourth in preparation. Two presentations were made at professional society meetings.

II. Technical Progress Report

A. Shock Tube Data System

The new data acquisition system for the NRL shock tube facility has made it possible to take full advantage of the multiple-detector capability of this unique facility. At the present time, three species can be monitored simultaneously in a single shock. Concentration profile algorithms for CO, NO, and H₂O absorption plus UV emission have been incorporated into the computer software, so that manual manipulations of the data are no longer required. A new high-resolution graphics and plotting system has been developed to improve the presentation of the data. Code optimization has increased the speed to the point where data analysis can be completed during the interval between successive shocks.

A new state-of-the-art tunable CW dye laser has been added to the two existing CO lasers dedicated to the shock tube facility, greatly increasing the versatility of the detection system. In addition, we have demonstrated the feasibility of using an optical multichannel analyzer to obtain spectral distributions and positive identification of emissions from transient species produced in the shock tube.

B. RRKM Studies of Combustion-related Free Radical Reactions

We have continued to augment the experimental program by performing TST-RRKM calculations, using a versatile program which can be adapted readily to a wide variety of reaction mechanisms. Our study of the reaction $\text{CH}_2 + \text{N}_2$,

described in the previous progress report, was accepted and has appeared in print.¹ The work on a comprehensive mechanism for $\text{CH}_3 + \text{C}_6\text{H}_5\text{O}$ has also been published.²

During this period we carried out a corrected and extended analysis of existing data on reactions of the NF_2 radical with a series of olefins, using the newly converted RRKM program. We provided new interpretations of the kinetic data and extracted additional information, including Arrhenius parameters for the apparent second order rate constants of the addition reactions $\text{NF}_2 + \text{olefin}$ and the apparent first order rate constants for the dissociation of the resulting adducts. As a by-product of the analysis we were able to obtain improved estimates of the unknown C-N bond energies in a number of alkyl difluoroamines.³ The complete mechanism was modeled by RRKM theory, including the addition of a second NF_2 radical to the initial adduct. The modeling also included complete pressure effects, using Troe's weak collision theory to estimate collisional energy transfer efficiencies.

C. Shock Tube Studies of the Reactions $\text{C}_6\text{H}_5 + \text{O}_2$ and $\text{C}_6\text{H}_5 + \text{NO}_2$

During this period we carried out an extensive series of kinetic experiments on the reactions of phenyl radical with O_2 and NO_2 , using the NRL shock tube facility. Data were obtained at temperatures ranging from 1000 K to 1500 K. The reaction rates were followed by monitoring the concentrations of CO and NO, using resonance or near-resonance absorption of CO laser radiation. Phenyl radicals were produced in the shock tube by decomposition of $\text{C}_6\text{H}_5\text{NO}$.

The analysis of these data is currently being carried out by kinetic modeling. Preliminary results for $C_6H_5 + O_2$ and NO_2 are:

$$k_{O_2} = 3 \times 10^{14} \exp(-10,000/T) \text{ cc/mole-sec}$$

$$k_{NO_2} = (0.1-5) \times 10^{12} \text{ cc/mole-sec}$$

These values depend strongly on the rate constant for the recombination of the C_6H_5 radical, which was assumed to be 3×10^{12} cc/mole-sec throughout the temperature region investigated. Because of the important role the C_6H_5 radical plays in soot formation chemistry, a direct determination of this rate is clearly called for.

D. Shock Tube Studies of the Reaction $O + C_6H_6$

The reaction of benzene with O atoms has been investigated by shocking mixtures of N_2O , NO_2 , and C_6H_6 in argon at temperatures in the range 1500-2000 K. Time-resolved CO, H_2O , and UV (254 nm) emission profiles have been determined. These data are also being analyzed by kinetic modeling.

Similar to the NO and CO kinetic measurements, the rate of H_2O formation described above was monitored by CO laser near-resonant absorption using the 8-7 P(15) line of the CO laser. The absorption calibration was made by using H_2O/Ar and $N_2O/H_2/Ar$ mixtures.

E. Kinetics of CH_3O Reactions at Intermediate Temperatures

A laboratory at CUA has been equipped for the study of reactions of CH_3O radicals at temperatures lower than those at which shock tube experiments are feasible. The primary system consists of static and stirred-flow reactors in thermostatted furnaces which allow the reactions to be carried out at temperatures up to approximately 500 °C. The CH_3O radicals are generated by thermal decomposition of an appropriate precursor and stable products are analyzed by a gas chromatograph. The detection system has been calibrated for CH_3ONO , CH_2O , and CH_3OH products, and initial experiments are in progress with the decomposition of CH_3ONO as the radical source. After the full and quantitative interpretation of the methyl nitrite system, olefins (eg., C_2H_2 and C_2H_4) will be added for the study of CH_3O + olefin reactions as proposed earlier.

A photon-counting system has also been set up in conjunction with a heated tubular reactor to monitor chemiluminescence from the reaction $\text{CH}_3\text{O} + \text{CH}_3\text{O} \longrightarrow \text{CH}_2\text{O}^* + \text{CH}_3\text{OH}$. Experiments are underway to generate CH_3O by $\text{CH}_3 + \text{CH}_3\text{O}_2$ using di-tert-butylperoxide as the CH_3 radical source. The CH_2O^* emission (~400 nm) profiles will be kinetically modeled and subsequently used to study CH_3O kinetics using CH_3ONO or CH_3OOCH_3 as the CH_3O source.

F. Publications

1. W. A. Sanders, C.-Y. Lin, and M. C. Lin, On the importance of the reaction $\text{CH}_2 + \text{N}_2 \longrightarrow \text{HCN} + \text{NH}$ as a precursor for prompt NO formation, Combust. Sci. and Tech., 51, 103 (1986).

2. C.-Y. Lin and M. C. Lin, The combination reaction of CH_3 and $\text{C}_6\text{H}_5\text{O}$, Aust. J. Chem., 39, 723 (1986).
3. W. A. Sanders and M. C. Lin, Kinetics and mechanism of reactions of NF_2 with olefins: Reinterpretation of existing data and estimation of C-N bond energies of alkyl difluoroamines, J. Chem. Soc. Faraday Trans. II, in press.

G. Presentations

1. C.-Y. Lin, W. A. Sanders, M. E. Umstead, and M. C. Lin, 21st International Symposium on Combustion, July 27-August 1, 1986, Munich, W. Germany.
2. S. C. Cooper, C.-Y. Lin, A. Argetsinger, and M. C. Lin, 1987 Fall Technical Meeting, The Combustion Institute, Eastern Section, December 14-17, 1986, San Juan, Puerto Rico.

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