Annual Report to
DOE Basic Energy Sciences
Fundamental Interactions Branch
Chemical Physics Program
on
**"Kinetics and Mechanisms of Reactions Involving
Small Aromatic Reactive Intermediates"**

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Summary

Phenyl (C_6H_5), phenoxy (C_6H_5O) and benzyne (C_6H_4) are fundamentally important prototype molecules. C_6H_5 and C_6H_5O are also very important reactive intermediates in hydrocarbon combustion systems, particularly with regard to soot formation chemistry, as well as to the combustion chemistry of aromatic additives in gasoline.

We proposed to study the kinetics and mechanisms of these three "benchmark" reactive intermediates using two complementary laser diagnostic techniques — laser resonance absorption (LRA) and resonance enhanced multiphoton ionization mass spectrometry (REMPI/MS). In the first year of this contractual work, we have employed a new type of LRA, i.e. the intra-cavity resonance absorption technique, to measure the rate constants for C_6H_5 reactions, extending the limit of rate constant measurement down to 10^{-18} cm³/s! We have tested this method for the following reactions: $C_6H_5 + HBr$, CH_2O , O_2 , C_2H_2 and C_2H_4 at 297 K and obtained their rate constants to be 3.0×10^{-11} , 1.2×10^{-14} , 1.0×10^{-16} , 7.0×10^{-18} and 6.7×10^{-18} cm³/s, respectively.

In the second study, the REMPI spectroscopy of C_6H_5 is being investigated with the two laser pump-probe surface photolysis method. The desorbed C_6H_5 photofragment is ionized by (1+1) MPI in the spectral range 220 - 260 nm. Similarly, the NO photofragment is also detected by (1+1) MPI in the same spectral region. The detailed photofragmentation of the absorbed C_6H_5NO at 193 and 248 nm is being analyzed presently and a new experiment with acetophenone on a quartz surface is under way.

In the coming year, we will focus our study on the temperature effect of C_6H_5 reactions with O_2 , C_2H_2 , C_2H_4 , C_6H_6 and CH_2O using both LRA and REMPI/MS methods. The results of these reactions are urgently needed for hydrocarbon combustion modeling.

Introduction

Small aromatic reactive intermediates such as C_6H_5 , C_6H_5O and C_6H_4 are important prototype species of their homologs. Both C_6H_5 and its oxidation product, C_6H_5O are believed to be important reactive intermediates which may play a pivotal role in hydrocarbon combustion chemistry, particularly with regard to soot formation chemistry under fuel-rich conditions.¹

Despite their fundamental importance, experimental data on the reaction mechanisms and reactivities of these C_6 -species are very limited. For C_6H_5 , most kinetic data except its reactions with NO and NO₂, were obtained by relative rate measurement.³⁻⁵ For C_6H_5O , we have earlier measured its fragmentation reaction producing $C_5H_5 + CO$ in shock waves.⁶ For C_6H_4 , the only rate constant measured in the gas phase is its recombination rate at room temperature by Porter and Steinfeld.⁷

We proposed to investigate systematically the kinetics and mechanisms of these important class of molecules using two parallel laser diagnostic techniques; laser resonance absorption (LRA) and resonance enhanced multiphoton ionization mass spectrometry (REMPI/MS).

The results obtained in the first year of this DOE supported study are briefly reported in the following section.

Accomplishments

I. LRA Measurements

In this past year, we have successfully employed a new type of intra-cavity resonance absorption method, which was originally developed by O'Keefe and Deacon who referred to it as "the cavity-ring-down" method.⁸ The experimental arrangement is shown in Fig. 1. The method lies in the measurement of photon decay

times within a highly reflective optical cavity with and without absorbing species. The presence of an absorbing species increases the loss coefficient and thus shortens the photon decay time within the cavity. Figure 2 shows the absorption spectrum of the C_6H_5 radical produced by the photodissociation of C_6H_5NO at 248 nm using the "cavity-ring-down" method. The two peaks appear at 504.9 and 505.1 nm agree with those observed by Porter and Ward using the flash photolysis method.⁹

We have utilized this method and applied it to kinetic studies for the first time. The result of this study is illustrated in figures 3 and 4. The evaluated rate constants for the reactions of C_6H_5 with HBr, CH_2O , O_2 , C_2H_2 and C_2H_4 are summarized in Table I, together with those reported in the literature using the conventional multipass absorption² and relative rate methods.⁵

II. REMPI/MS Study

In order to characterize the REMPI spectroscopy of the C_6H_5 radical in the 220 - 260 nm region, we have investigated the photodissociation of C_6H_5NO on a (1120) sapphire surface. The major desorbed photofragments detected, in addition to C_6H_5 and NO, are C_6H_4 , C_6H_6 and C_4H_2 . Both C_6H_5 and NO have been ionized by (1+1)MPI in the 220-260 nm region. NO vibrational excitation was detected up to $v=3$. For NO ($v=0$), the rotational temperature was measured to be 203 K at 90 μ sec and 400 K at 180 μ sec time-of-flight (TOF) peaks, respectively.

Currently, we are in the process of analyzing the detailed product TOF distributions as well as the ro-vibrational distribution of the NO formed in the photofragmentation reaction. Two papers on the surface photochemistry of C_6H_x species and NO formation dynamics will be prepared for publication.

III. Publications.

1. "Detection and Kinetics of the Phenyl Radical: Tests for a New Intra-Cavity Absorption Method", M. C. Lin and T. Yu, in preparation.
2. "Photo-fragmentation of Adsorbed C_6H_5NO on Al_2O_3 (11 $\bar{2}0$): Reactions of the C_6H_5 Radical", S.-P. Lee and M. C. Lin, in preparation.
3. "Photo-fragmentation of Adsorbed C_6H_5NO on Al_2O_3 (11 $\bar{2}0$): Dynamics of NO Desorption", S.-P. Lee and M. C. Lin, in preparation.

IV. Presentations

1. "KrF Laser-induced Photochemistry of Nitrosobenzene Adsorbed on a Cold Al_2O_3 (11 $\bar{2}0$) Surface: Desorption Dynamics of the NO Photofragment" S.-P. Lee and M. C. Lin, XXth Informal Conference on Photochemistry, April 26-May 1, 1992, Atlanta, Ga.
2. "Application of the Cavity-Ring-Down Method to Studies of Nonfluorescing Free Radical Reactions: A Test for C_6H_5 ", T. Yu and M. C. Lin, 1992 Fall ACS National Meeting Aug. 23-28, 1992, Washington D. C. (accepted).
3. "Kinetic Spectroscopy for Non-fluorescing Free Radical Reactions" M. C. Lin, T. Yu, S.-P. Lee and J. A. Tarr, 6th International Symposium on Organic Free Radicals, Aug. 23-28, 1992, Noordwijkerhout, The Netherlands (accepted).

Future Plans:

1. Complete characterization of the C_6H_5 REMPI spectroscopy and apply it for kinetic measurements: $\text{C}_6\text{H}_5 + \text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{O} + \text{O}$
2. Temperature dependence measurements with the intra-cavity resonance absorption method for the following reactions at $297 \leq T \leq 650 \text{ K}$:
 - a. $\text{C}_6\text{H}_5 + \text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{O} + \text{O}$
 - b. $\text{C}_6\text{H}_5 + \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_5\text{C}_2\text{H} + \text{H}$
 - c. $\text{C}_6\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow \text{C}_6\text{H}_5\text{C}_2\text{H}_3 + \text{H}$
 - d. $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_6 \rightarrow (\text{C}_6\text{H}_5)_2 + \text{H}$
 - e. $\text{C}_6\text{H}_5 + \text{CH}_2\text{O} \rightarrow \text{C}_6\text{H}_6 + \text{CHO}$.

The absolute rate constant measurements for these reactions have never been accomplished before.

References

1. I. Glassman, Combustion, 2nd Ed., Academic Press, 1987.
2. M. Preidel and R. Zellner, B. Bunsenges. Phys. Chem., 93, 1417 (1989).
3. J. A. Kerr and S. J. Moss, Handbook of Bimolecular and Termolecular Gas Reactions, CRC Press, Boca Raton, FL., 1981.
4. A. Fahr, W. G. Mallard and S. E. Stein, 21st Symp. (Int.) on Combustion, p. 825, 1986.
5. A. Fahr and S. E. Stein, 22nd Symp. (Int.) on Combustion, p. 1023, 1988.
6. C.-Y. Lin and M. C. Lin, J. Phys. Chem. 90, 425 (1986).
7. G. Porter and J. Steinfeld, J. Chem. Soc., (A) 377 (1968).
8. A. O'Keefe and D. A. G. Deacon, Rev. Sci. Instrum., 59, 2544 (1988).
9. G. Porter and B. Ward, Proc. Roy. Soc. A287, 457 (1965).

Table I. Rate constants (in units of cm^3/s) for C_6H_5 reactions with selected molecules at room temperature (297 K).

Reactant	This Study	Preidel and Zellner ^a	Fahr and Stein ^b
HBr	3.0×10^{-11}	—	—
CH_2O	1.2×10^{-14}	—	—
O_2	1.0×10^{-16}	$\leq 10^{-17}$	—
C_2H_2	7.0×10^{-18}	$\leq 8 \times 10^{-16}$	(2.4×10^{-16})
C_2H_4	6.7×10^{-18}	$\leq 8 \times 10^{-17}$	(1.1×10^{-16})
C_6H_6	—	$\leq 3 \times 10^{-15}$	(2.9×10^{-18})
NO	—	1.1×10^{-11}	—
NO_2	—	8.2×10^{-12}	—

a. M Preidel and R. Zellner (Ref. 2)

b. A. Fahr and S. Stein (Ref. 5); extrapolated from data obtained above 1000 K.

Figure 1. The New Intracavity Resonance Absorption (or Cavity-Ring-Down) Apparatus.

Absorption spectrum of Phenyl Radical

Figure 2. Absorption Spectrum of C_6H_5 obtained by the ICRA Method.

Typical decay plot of Phenyl + O₂

Figure 3. Pseudo-First-Order Plots for C₆H₅ + O₂ at Various O₂ Concentrations.

Arrhenius plot of C₆H₅ + XYZ at 297K

Figure 4. Second-Order Rate Constant Plots for C₆H₅ + HBr, CH₂O and C₂H₂.

The Concentration of HBr and CH₂O were scaled by the factor indicated.

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