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"Kinetics of Elementary Processes Relevant to Incipient Soot Formation"

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Summary

In order to better understand the mechanism of soot formation (one of the most challenging problems in the study of hydrocarbon combustion chemistry), reliable rate constants for the key reaction steps involved in the formation and polymerization of aromatic hydrocarbons in the inception stage are required for kinetic modeling. In this DOE sponsored work, we have developed three new experimental methods: cavity ring-down (CRD) spectrometry, pyrolysis/Fourier transform infrared spectrometry (p/FTIRS) and pulsed laser photolysis/mass spectrometry (PLP/MS) for kinetic measurements of C_6H_5 reactions pivotal to incipient soot formation chemistry. In addition, we have also carried out ab initio molecular orbital (MO) calculations for several key elementary combustion reactions relevant to soot formation.

The results of our studies have been presented at 16 national and international conferences and also published in 22 technical papers. These results are briefly summarized in the report using selected examples for more detailed discussion.

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I. Introduction

Understanding the chemistry of soot formation in its incipient stages remains one of the most challenging and fundamentally interesting problems in the study of fossil fuel combustion processes. The chemistry involved in the formation of the first few rings of polycyclic aromatic hydrocarbons (PAH's), precursors to soot, is complex and the phenyl radical is believed to play a key role in the formation of naphthalene and larger PAH's by reactions with acetylene and other unsaturated hydrocarbons.¹⁻³

In order to elucidate the mechanism of the formation of PAH's, which requires reliable kinetic data for the reactions of aromatic radicals of varying sizes with combustion species, in the past few years we have developed a new multipass laser absorption technique, originally referred to as the cavity-ring-down (CRD) method,^{4,5} for kinetic studies of aromatic radical reactions.^{6,7} The CRD technique, as briefly reviewed in a report by Wilson in the Chemical and Engineering News,⁸ has a sensitivity which rivals that of laser-induced fluorescence (LIF). By means of the CRD, tailored for radical decay kinetic studies, we measured the absolute rate constants for numerous C_6H_5 and C_6H_5O reactions⁹⁻¹⁵ up to 523 K, beyond which the well-known temperature-broadening of rovibronic absorption renders reliable diagnostics difficult for these large free radicals.

During this funding period (Jul 15, 1991-July 31, 1997), we have developed three new experimental approaches: The cavity ringdown spectrometry, pyrolysis/FTIR spectrometry and pulsed laser-photolysis/mass spectrometry and applied them to obtain complementary kinetic data for C_6H_5 radical reactions up to 1000 K. The new kinetic data acquired by these techniques will be presented in this report and potential kinetic measurements for other key combustion species such as C_2H_3 will be discussed.

The most important initiative embarked on at Emory University during this funding period lies perhaps in our strengthened, parallel effort in ab initio molecular

orbital (MO) calculations for the mechanistic elucidation of complex reactions relevant to incipient soot chemistry. The results of these studies are reported herein and future research opportunities in this area will also be presented and discussed.

II. Accomplishments (1991-1997)

A. Experimental Studies

As alluded to in the Introduction, three complementary experimental methods have been employed in this funding period for the kinetic measurement of C_6H_5 and C_6H_5O radical reactions of relevance to the formation of PAH's. The results of these studies are briefly summarized below.

1. Kinetic measurements by CRD:

The advantage and the experimental procedure of the CRD technique for the detection of weak-absorbing aromatic species in the visible region was discussed in detail and the preliminary kinetic data for the reactions of C_6H_5 with HBr/DBr ,^{7,9} NO ,¹⁰ C_2H_2 ¹¹ and C_2H_4 ¹² have been presented in several papers as referenced.

During this funding period, we have fully elucidated the kinetics and mechanism of the $C_6H_5 + O_2$ reaction,¹³ aided by ab initio MO calculations for the energies of 14 geometric isomers of $C_6H_5O_2$ ¹⁶ (vide infra). The rate constant for $C_6H_5 + O_2$ measured between 297 and 473 K at 20-80 torr pressure, $k_{O_2} = 10^{-11.00 \pm 0.08} e^{(161 \pm 66)/T}$ cm³/molecule-s, was found to be pressure-independent. The reaction results in the formation of the C_6H_5OO radical below 1000 K according to the prediction of a preliminary RRKM calculation for the conditions employed.¹³ At higher temperatures and low pressures, the reaction can produce $C_6H_5O + O$ and possibly C_6H_4 (o-benzyne) + HO_2 and OC_6H_4O (o-benzoquinone) + H based on the detailed results of our ab initio MO/RRKM calculations for the analogous $C_2H_3 + O_2$ reaction to be discussed later. Frank et al.¹⁷ reported the kinetics of O- and H-atom formation which may be attributable to the appearance of these product channels above 1000 K

in shock waves. The quantitative calculation of their rate constants requires an appreciable computational effort for the potential energy surface of the $\text{C}_6\text{H}_5 - \text{O}_2$ system. We will carry out such a study in the near future.

For C_6H_5 , we have also investigated the kinetics of its abstraction reactions with CCl_4 , $\text{c-C}_5\text{H}_{10}$, $\text{c-C}_6\text{H}_{12}$, $\text{c-C}_7\text{H}_{14}$, and $\text{c-C}_8\text{H}_{16}$.¹⁴ With the first three molecules, which have been employed as solvents as well as the reference standards of many C_6H_5 reactions in solution using the relative rate method,¹⁸⁻²¹ we have obtained their absolute rate constants by CRD covering 297-523 K, given in units of $\text{cm}^3/\text{molecule}\cdot\text{s}$:

$$k_{\text{CCl}_4} = 10^{-11.70 \pm 0.05} e^{-(1379 \pm 56)/T}$$

$$k_{\text{c-C}_5\text{H}_{10}} = 10^{-11.35 \pm 0.08} e^{-(2039 \pm 66)/T}$$

$$k_{\text{c-C}_6\text{H}_{12}} = 10^{-11.10 \pm 0.24} e^{-(1913 \pm 191)/T}$$

The results compare reasonably well with those determined by the relative method when our absolute rate constants for the reference reactions were employed in the calculation of absolute values from the reported rate constant ratios.¹⁴ Similarly for $\text{c-C}_7\text{H}_{14}$ and $\text{c-C}_8\text{H}_{16}$, the values of rate constants determined at 333 K, 8.2×10^{-14} and 9.0×10^{-14} , respectively, agree closely with those measured by the relative rate method using $\text{C}_6\text{H}_5 + \text{CCl}_4 \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{CCl}_3$ as the reference reaction in solution. Our absolute rate constants for $\text{C}_6\text{H}_5 + \text{CCl}_4$, $\text{c-C}_5\text{H}_{10}$ and $\text{c-C}_6\text{H}_{12}$ can be used to derive absolute rate values for numerous reactions studied in solution.¹⁸⁻²⁰

The CRD method was also employed for the determination of the rate constant for the $\text{C}_6\text{H}_5\text{O} + \text{NO}$ association reaction:

$k_r = 10^{-12.12 \pm 0.24} e^{+(194 \pm 185)/T} \text{ cm}^3/\text{molecule}\cdot\text{s}$.¹⁵ The $\text{C}_6\text{H}_5\text{O}$ was found to have a strong rovibronic transition in the 550-600 nm region and our measured spectrum agrees closely with the broad transition reported by Ward using the conventional flashphotolysis technique.²²

The $\text{C}_6\text{H}_5\text{O} + \text{NO}$ association reaction was found to be highly reversible because of the weak $\text{C}_6\text{H}_5\text{O}-\text{NO}$ bond. In order to differentiate the relative stability of phenyl nitrite and the nitrosophenoxy, $\text{O}=\text{C}_6\text{H}_5\text{NO}$, we performed ab initio MO calculations at the MP4(SDQ)/6-31G(d) level of theory using HF optimized geometries. The structures and energies of five $\text{C}_6\text{H}_5\text{N}_1\text{O}_2$ isomers were calculated. Among them, the most stable association product, $\text{C}_6\text{H}_5\text{ONO}$, was found to be 17 kcal/mole below the reactants. Combining the measured rate constant and the calculated equilibrium constant for the association reaction, the rate constant for the unimolecular decomposition of $\text{C}_6\text{H}_5\text{ONO}$ was obtained as $k_d = 4.6 \times 10^{15} e^{-8,580/T} \text{ s}^{-1}$. The A-factor appears to be reasonable for the decomposition process. Table I summarizes all existing C_6H_5 kinetic data determined by us with the CRD technique.

Kinetic measurements for C_6H_5 and $\text{C}_6\text{H}_5\text{O}$ radical reactions are still underway. Unfortunately, during the past year, both the photodissociation excimer laser (Lambda-Physik LPX-100) and the probing dye Laser (Laser Photonics, N_2 -laser-pumped dye laser), which were provided fully by Emory University for the DOE-sponsored project, suffered component breakdowns and both required long and extensive repairs. This expensive (time- and cost-wise) delay significantly set back our original plan of completing the initial phase of kinetic measurements of the C_6H_5 radical reactions by CRD with the key classes of organic compounds of relevance to combustion: alkanes, alkenes, alkynes, aldehydes, alcohols, amines and small arenes up to 523 K. This ambitious goal cannot be achieved without the support for a new and reliable photodissociation laser and/or a durable probing dye laser as well.

2. Kinetic studies by pyrolysis/FTIR spectrometry

The CRD spectrometric technique is limited to the determination of bimolecular rate constants $\geq 10^{-16} \text{ cm}^3/\text{molecule}\cdot\text{s}$ (similarly to LIF) at temperatures of $T \leq 523 \text{ K}$ due to the temperature broadening of rotational populations as mentioned earlier. To compensate for that deficiency, we have developed a chemical reaction system for

kinetic studies of C_6H_5 reactions using C_6H_5NO as the thermal source of the phenyl radical. For this purpose, we have determined the rate constant for the unimolecular decomposition of C_6H_5NO :

by monitoring the decay of C_6H_5NO and the production of NO by FTIR spectrometry using highly diluted C_6H_5NO/Ar mixtures under atmospheric pressure conditions.²³ Kinetic modeling of the measured data by including minor secondary reactions, such as $C_6H_5 + C_6H_5NO \rightleftharpoons (C_6H_5)_2NO$ and $C_6H_5 + C_6H_5 \rightarrow C_{12}H_{10}$, for which we have recently determined their absolute rate constants (vide infra), gave rise to

$$k_{C_6H_5NO} = 1.4 \times 10^{17} e^{-27,730/T} \text{ s}^{-1}.$$

for the temperature range of 550-650 K. These data are compared in Fig. 1 to that of Choo et al. measured by the very low pressure pyrolysis (VLPP) technique,²⁴ as well as that of Horn and coworkers, determined at higher temperatures using a flow reactor and a shock tube.²⁵ Our significantly larger activation energy, 55 ± 1 kcal/mole, appears to be in good agreement with the bond energy predicted by C. F. Melius with the BAC-MP4 technique, 57.6 kcal/mole at 300 K (private communication). We plan to perform a higher level MO calculation for the decomposition process.

The establishment of the C_6H_5NO decomposition kinetics in the 550-650 K range enables us to carry out rate constant measurements for bimolecular reactions of C_6H_5 with H_2 , CH_4 and other alkanes which are too slow to be measured by the CRD technique. These reactions are directly relevant to the formation of C_6H_5 by $R + C_6H_6 \rightarrow RH + C_6H_5$, where $R = H, CH_3, C_2H_5$, etc. To date, we have completed the preliminary measurement for the abstraction reaction:

by monitoring both the decay of C_6H_5NO and the growth of C_6H_6 in the pyrolysis of highly diluted C_6H_5NO/H_2 mixtures. The kinetic modeling of the time-resolved concentration profiles of both species using a mechanism which includes HNO as a likely reaction

intermediate (from $\text{H} + \text{NO} + \text{M} = \text{HNO} + \text{M}$, $\text{H} + \text{C}_6\text{H}_5\text{NO} = \text{C}_6\text{H}_5 + \text{HNO}$, a near-heat-neutral process) enables us to deduce with high sensitivity and reproducibility the rate constant for the $\text{C}_6\text{H}_5 + \text{H}_2$ reaction. The result of this study are presented in Fig. 2 and compared to literature values²⁶⁻³¹ (most of which were calculated from kinetically modeled rate constants for the reverse process, $\text{H} + \text{C}_6\text{H}_6 \rightarrow \text{H}_2 + \text{C}_6\text{H}_5$ obtained by shock tube studies). Also included in the figure are our theoretically predicted value and the result obtained by PLP/MS;³² both are to be presented below. The agreement between theory and our latest experiments is excellent.

3. Pulsed laser photolysis/mass spectrometric studies

Another versatile experimental technique developed for kinetic measurements during this funding period is PLP/MS employing the high-pressure sampling method of Saalfeld and coworkers.³³ The sampling method had been successfully utilized by Gutman, Slagle and coworkers, in conjunction with pulsed laser photolysis and vacuum UV photo-ionization mass spectrometry for kinetic measurements of free radical reactions.^{34,35} In our experimental arrangement,³⁶⁻³⁹ either electron-impact ionization mass spectrometry (EI/MS) or resonance-enhanced multiphoton ionization mass spectrometry (REMPI/MS) can be employed for product or reactant diagnostics. For the reactions of interest to incipient soot formation, we employed EI/MS for the time-resolved detection of such C_6H_5 reaction products as C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$ and $\text{C}_{12}\text{H}_{10}$ (biphenyl), as will be illustrated by our investigation of the C_6H_5 recombination and $\text{C}_6\text{H}_5 + \text{H}_2$ kinetics.

$\text{C}_6\text{H}_5 + \text{C}_6\text{H}_5$: The recombination reaction of C_6H_5 radicals plays a pivotal role in the oxidation of benzene at high temperatures and in earlier studies of C_6H_5 kinetics by the relative rate method. The role of the C_6H_5 recombination reaction in the benzene oxidation process is similar to that of $\text{CH}_3 + \text{CH}_3$ in the CH_4 oxidation process at high temperatures. These recombination reactions strongly affect the concentrations of the radicals and thus the overall oxidation rates of the systems of interest.

Prior to the inception of our study on the kinetics of the C_6H_5 recombination reaction by PLP/MS in February 1996, there were no reports of the experimentally measured rate constant. It had been assumed chronologically to range from 1.7×10^{-10} to 5.0×10^{-12} $cm^3/molecule \cdot s$.⁴⁰⁻⁴² This large range of assumed values affects the rate constants for many phenyl reactions studied over the years by the relative method using the recombination reaction as the reference process.³⁹⁻⁴²

In our present study by PLP/MS, we photolyzed C_6H_5NO at 248 nm at 5-7 torr pressure using He as the carrier gas. By measuring precisely the amount of C_6H_5NO fragmented and the concentration of $C_{12}H_{10}$ formed in the presence of varying amounts of added NO, we determined reproducibly the rate constants of the two key processes occurring in the system:³⁹

with

$$k_{C_{12}H_{10}} = (2.3 \pm 0.2) \times 10^{-11} e^{-(56 \pm 36)/T}$$

$$k_{(C_6H_5)_2NO} = (8.1 \pm 0.3) \times 10^{-12} e^{+(34 \pm 16)/T} \text{ cm}^3/\text{molecule} \cdot s,$$

over the temperature range of 300-500 K. The formation of stable biphenyl nitroxide was supported by mass balance as well as the appearance of $m/z 184$.³⁹ Our phenyl recombination result is presented in Fig. 3 in comparison with those reported by Just,²⁵ Troe³⁰ and their collaborators at the latest International Symposium on Combustion (held in Naples, Italy, July 28-August 2, 1996), 5×10^{-11} and 1×10^{-11} $cm^3/molecule \cdot s$, respectively, measured in shock waves above 1000 K.

$C_6H_5 + H_2$: With the PLP/MS technique, we have also attempted to measure the rate constant for $C_6H_5 + H_2$ above 650 K, which is the upper limit of temperature amenable to the pyrolysis/FTIR kinetic measurement with C_6H_5NO as the C_6H_5 source as discussed above. By photolyzing $C_6H_5COCH_3$ at 193 nm, we can study the reaction of C_6H_5 with H_2 and other RH molecules ($R = CH_3, C_2H_5$, etc.) up to 900 K,

above which the thermal decomposition of the C_6H_5 precursor may complicate the kinetics.

The measured $C_6H_5 + H_2$ data are included in Fig. 2 for comparison with the calculated result; the agreement between theory and experiment appears to be excellent. For the $C_6H_5 + CH_3$ recombination reaction, our value $k_b = 2.3-2.5 \times 10^{-11}$ $cm^3/molecule \cdot s$ also agrees closely with the recommended rate constant by Tsang and Kiefer⁴³ given by the expression $k_b = 2.3 \times 10^{-10} T^{-0.3}$ $cm^3/molecule \cdot s$, which predicts $k_b = 3.2 \times 10^{-11} - 3.1 \times 10^{-11}$ $cm^3/molecule \cdot s$ at 701-833 K. These and other data recently obtained by PLP/EI-MS on $C_6H_5 + C_6H_5$ ³⁹ and the product branching ratios for the $NH_2 + NO_x$ reactions³⁶⁻³⁸ have amply demonstrated the versatility of the technique with EI-MS. The implementation of the REMPI/MS diagnostics for the detection of those radical reactants which can be resonantly ionized (the option which is readily available in our system) could provide additional kinetic data for cross-checking.

B. Theoretical Studies

The lowering of computational cost in the past several years and the availability of many efficient commercial software packages such as Gaussian⁴⁴ and MOLPRO⁴⁵ programs, enabled us to carry out extensive high-level ab initio MO calculations for systems containing as many as seven heavy atoms.⁴⁶ The results of these calculations are often revealing and useful for the elucidation of the complex mechanisms involved in the reactions of interest to incipient soot chemistry. During this funding period, we have investigated several reaction systems containing four or more heavy atoms: $C_2H_3 + O_2$,⁴⁷ $CH_3 + C_5H_5$,⁴⁸ the unimolecular decomposition reactions of C_6H_5 ⁴⁹ and C_6H_5O ,⁵⁰ $C_6H_5 + H_2$ and $H + C_6H_6$,⁵¹ $C_6H_5 + O_2$ ¹⁶ and $O + C_6H_5O$.⁵² The results of these calculations are summarized below:

1. $C_2H_3 + O_2 \rightarrow products$

C_2H_3 reactions are relevant to the formation of the first aromatic ring, directly or indirectly.^{1,3} The reaction of C_2H_3 with O_2 competes with its reaction with C_2H_2 , thus potentially reducing the formation of PAH's and soots.

In our calculations, we employed a modified Gaussian-2 method (G2M) scheme developed at Emory University.⁴⁶ This scheme is a modification of the Gaussian 2 (G2) approach by Pople and coworkers,⁵³ employing the B3LYP method (i.e., Becke's three-parameter nonlocal-exchange functional⁵⁴ with the nonlocal correlation functional of Lee, Yang and Parr⁵⁵) to optimize the geometries of the reactants, products and transition states using the 6-311G(d,p) basis set. All vibrational frequencies were also computed using the B3LYP/6-311G(d,p) level of theory and employed for zero-point energy (ZPE) corrections and statistical-theory calculations without further scaling.⁴⁶ For more reliable energy calculations of key intermediates and transition states involved in the reactions, different G2M schemes were used (depending on the number of heavy atoms involved) to approximate the QCISD(T)/6-311G(d,p) calculation of the original G2 scheme⁵³ by the restricted open-shell coupled cluster⁴⁵ RCCSD(T)/6-311G(d,p) calculation.⁴⁶ A more detailed description of the G2M method can be found in Ref. 46 and the additional applications of the method for the individual systems are discussed below.

The potential energy surface (PES) of the $C_2H_3 - O_2$ system, computed with the G2M(RCC,MP2) scheme is shown in Fig. 4. The most favorable reaction pathway leading to the major products, $CHO + CH_2O$, is as follows: $C_2H_3 + O_2 \rightarrow C_2H_3OO$ **1** or **1'** $\rightarrow$ **TS8** $\rightarrow$ dioxiranylmethyl radical **3** $\rightarrow$ **TS9'** $\rightarrow$ oxiranyloxy radical **10** $\rightarrow$ **TS11** $\rightarrow$ formyloxy methyl radical **12'** $\rightarrow$ **TS13'** $\rightarrow$ $CHO + CH_2O$, where the rate-limiting step is the terminal O-atom migration to the CC bridging position via **TS9'**, which lies 14.3 kcal/mole below the reactants. The $C_2H_3O + O$ products can be formed by eliminating the terminal O atom from C_2H_3OO via **TS23**, which lies 7.8 kcal/mole below the reactants. The formation of another key pair of the products, $C_2H_2 + O_2H$, can take

place directly via **TS25'** from **1'**. The stepwise alternative via **TS25** and **TS27**, having a positive barrier of 3.9 kcal/mole, is much less competitive.

A multichannel RRKM calculation including two reversible steps as given by the scheme:

gave rise to the following key rate constants (in units of $\text{cm}^3/\text{molecule}\cdot\text{s}$) for 300-3500 K at 760 torr N_2 pressure:⁴⁷

$$k_{\text{tot}} = 9.15 \times 10^{-13} T^{0.23} e^{+454/T}$$

$$k_g + k_e = 7.6 \times 10^{-8} T^{-1.39} e^{-511/T} (\text{CHO} + \text{CH}_2\text{O})$$

$$k_b = 5.0 \times 10^{-13} T^{0.29} e^{-5.4/T} (\text{C}_2\text{H}_3\text{O} + \text{O})$$

$$k_d = 2.2 \times 10^{-18} T^{1.61} e^{+193/T} (\text{C}_2\text{H}_2 + \text{O}_2\text{H})$$

$$k_h = 5.1 \times 10^{-11} T^{-8.00} e^{-2861/T} (\text{C}_2\text{H}_3\text{OO})$$

These results are recommended for the kinetic modeling of high-temperature hydrocarbon combustion processes. The detailed mechanism should also serve as a model for the $\text{C}_6\text{H}_5 + \text{O}_2$ reaction, discussed below. It should be mentioned that in our calculation of the association reaction (a), whose transition state is undefined quantum mechanically, we used the canonical variational transition-state theory (CVTST)⁴⁷ method to locate its position along the reaction coordinate with the maximum G at each temperature. The molecular structures and frequencies determined at various temperatures were employed individually for the RRKM calculations.

The predicted total rate constant for $C_2H_3 + O_2$, k_{tot} (which is pressure-independent below 760 torr), given above agrees quantitatively with the data reported by Gutman, Slagle, Laufer, and their collaborators.⁵⁶⁻⁵⁸

2. *Recombination of CH_3 with C_5H_5 :*

CH_3 and C_5H_5 are stable radicals whose reaction near sooting conditions may generate (or regenerate) C_6H_6 .⁴⁸ In order to elucidate the mechanism of the $CH_3 + C_5H_5$ reaction, we performed ab initio MO calculations at the G2M(rcc,MP2) level of theory.⁴⁶ The computed PES presented in Fig. 5 indicates that the bond energy, $D(CH_3 - C_5H_5)$, is 72 kcal/mole and the $CH_3 + C_5H_5$ reaction can directly produce $C_5H_4CH_3 + H$ with an endothermicity of only 7.6 kcal/mole. The methylcyclopentadienyl thus formed, $C_5H_4CH_3$, can dissociate to generate fulvene ($C_5H_4CH_2$) with an activation energy of ~47 kcal/mole. Other, less favorable reaction paths, including the molecular process $CH_3 + C_5H_5 \rightarrow \text{fulvene} + H_2$, were also calculated.⁴⁸ It is worth noting that the heats of formation of various species shown in the figure agree closely with those predicted by Melius et al. with the BAC-MP4 method.⁵⁹ These results suggest that $CH_3 + C_5H_5$ may be a source of fulvene and its isomer, benzene, at high temperatures. The isomerization of fulvene to benzene has also been computed with the G2M(rcc,MP2) method;⁶⁰ our result supports quantitatively the mechanism proposed by Melius and coworkers calculated with the BAC-MP4 method.^{59,61} The details of our calculation, which can be found in ref. 60, will not be discussed here because of space limitations.

3. *Unimolecular decomposition of C_6H_5 and o - C_6H_4*

The kinetics and mechanism of phenyl radical decomposition are pivotal to our understanding of the incipient soot formation process and the combustion of gasoline in which small aromatics are used as additives. It has been commonly assumed that C_6H_5 decomposes at high temperatures by the ring-opening process producing a linear isomer, I - C_6H_5 , which then fragments to give smaller species;^{28,29,62-66}

Although these processes can occur in principle,^{65,66} the overall endothermicities (and activation energies) are very high and kinetically cannot compete with the production of o-C₆H₄ (benzyne) + H, whose reverse barrier was calculated to be zero:⁴⁹

At the G2M(rcc,MP2) level of theory,⁴⁹ the dissociation energy for the H atom formation was computed to be 76.0 kcal/mole, which is comparable to the ring-opening barrier of 72 kcal/mole reported by Walch using the RHF/cc-pVDZ technique.⁶⁶ Since the decomposition of I-C₆H₅ to produce I-C₆H₄ + H and C₂H₂ + C₄H₃ requires an additional 40 kcal/mole of activation energy,^{49,66} most thermally activated I-C₆H₅ radicals cyclize back to phenyl with a small (~6 kcal/mole) activation energy^{49,66} and the excited C₆H₅ thus formed, fragments to yield o-C₆H₄ + H with a near-unity probability in comparison with the formation of C₂ and C₄ species. The energy diagram for the C₆H₅ system obtained at the G2M(rcc,MP2) level of theory is presented in Fig. 6. Our predicted ring-opening barrier is 6 kcal/mole lower than that of Walch's value, although the overall barrier producing C₄H₃ + C₂H₂, 105.6 kcal/mole agrees closely with his result, 109.6 kcal/mole.⁶⁶

On account of the absence of the reverse barrier for reaction (d), i.e., E_{-d} = 0, a canonical variational calculation has been carried out to obtain k_d using the equation:

$$k_d = \frac{kT}{h} e^{-\Delta G^\ddagger / RT}$$

For 500-3000 K, k_d = 2.7 × 10¹⁵ e^{-37,850/T} s⁻¹, which corresponds to the rate constant for the decomposition of C₆H₅ at infinite pressure. For the calculation of the rate constant of the decomposition reaction under combustion conditions, a special RRKM

program is being prepared to compute all coupled reaction channels, as in the case of $C_2H_3 + O_2$. These results are being prepared for publication in the near future.

We have also calculated the rate constant for the unimolecular decomposition of o-benzyne with the G2M(rcc,MP2) method.⁴⁹ The decomposition reaction producing $C_4H_2 + C_2H_2$ was found to have a well-defined barrier, 87 kcal/mole. The details of this system with the predicted rate constant as a function of temperature and pressure with the RRKM theory will be prepared for publication shortly.

4. Unimolecular decomposition of C_6H_5O

The phenoxy radical is a key intermediate of the oxidation of benzene and toluene;^{1,3} it can be produced readily from $C_6H_5 + O_x$ and HO_x ($x=1,2$) reactions. The kinetics of the unimolecular decomposition reaction⁶⁷⁻⁷⁰

has been investigated extensively by us as well as by Just and coworkers in shock waves over a wide range of temperature (1000-1700 K).^{17,70} The apparent activation energy for the decomposition reaction was found to be 44 kcal/mole in both studies.

The mechanism for the decomposition process has been studied theoretically, independently by Olivella et al.⁷¹ and by the PI in collaboration with the Morokuma group at Emory University.⁵⁰ In our calculations, we employed the G2M(rcc,MP2) method and identified four possible intermediates and six transition states. One intermediate $I-O=CCHCHCHCHCH$, derived from the ring-opening process, has a significantly higher barrier than those calculated for the formation and fragmentation of the bicyclo-intermediate formed by bridging the two α -carbon atoms neighboring the CO group.^{50,71} The rate-determining step lies in the opening of the three-membered ring, TS2, as shown below:

A multistep RRKM calculation based on the above favored reaction path gave the apparent high-pressure activation energy of 52 kcal/mole,⁵⁰ which is 8 kcal/mole greater than the experimentally measured value.^{17,70} Further analysis and modeling of experimental data are required to reconcile this large deviation.

5. $\text{C}_6\text{H}_5 + \text{H}_2$ and $\text{H} + \text{C}_6\text{H}_6$ reactions

The two related reactions:

have been studied experimentally rather extensively,^{26-32,72-78} particularly the addition reaction (b) which occurs more readily at low temperatures.

We have calculated the PES of the $\text{C}_6\text{H}_5 - \text{H}_2$ system, the simplest phenyl abstraction reaction, and used the computed transition state parameters to calculate thermal rate constants for both above reactions.⁵¹ For the direction abstraction (a), the energy barrier was calculated to be 8.8 kcal/mole at our best G2M(rcc,MP2) level of theory with the tunneling corrected TST rate constant, $k_a = 9.5 \times 10^{-20} T^{2.43} e^{-3159/T} \text{ cm}^3/\text{molecule}\cdot\text{s}$ covering 300-5000 K.⁵¹ The theoretical curve is presented in Fig. 2 to be compared with literature data, some of which have been computed from kinetically modeled reverse rate constant, k_{-a} , using the experimental heat of reaction $\Delta H_a^\circ = -8.7$ kcal/mole, as mentioned before. Our predicted exothermicity is 2.1 kcal/mole smaller. As shown in Fig. 2, the theoretical rate constant for $\text{C}_6\text{H}_5 + \text{H}_2$ lies approximately in the

middle of experimental scatters and agrees closely with our values obtained from $\text{C}_6\text{H}_5\text{NO} + \text{H}_2$ by pyrolysis/FTIR spectrometry and PLP/MS mentioned above. At high temperatures, the result of Kiefer et al.,²⁹ computed from their reverse rate constant, also agrees well with the predicted value.

In Fig. 7, we compare the predicted, pressure- and temperature-dependent rate constants for reaction (b), the addition of H to C_6H_6 , with experimentally measured values obtained within the 1-100 torr pressure range. Our predicted curves for 1 and 100 torr effectively encompass all existing data. In our calculations using the RRKM theory, the theoretical barrier, 8.9 kcal/mole, was used with tunneling corrections. It is worth noting that the addition barrier is about twice as large as that for $\text{H} + \text{C}_2\text{H}_4$, 4.7 kcal/mole.⁷⁹

6. $\text{C}_6\text{H}_5 + \text{O}_2$ and $\text{O} + \text{C}_6\text{H}_5\text{O}$ reactions

In order to interpret and extrapolate the absolute rate constant obtained by the CRD method and reported in the preceding section,

we performed a preliminary calculation¹⁶ of the structural isomers of $\text{C}_6\text{H}_5\text{OO}$ at the spin-projected MP3/6-31G(d) level of theory. The result of this calculation identified 14 structural isomers including the initial adduct, $\text{C}_6\text{H}_5\text{OO}$, the $\text{C}_6\text{H}_5\cdots\text{O}_2$ π -complex, three $\text{C}_6\text{H}_4(\text{O})\text{OH}$, four $\text{OC}_6\text{H}_5\text{O}$ radicals, three epoxy isomers, $\text{C}_6\text{H}_4\text{OOH}$, and a seven-membered ring $\text{C}_6(\text{O})\text{H}_5\text{O}$ radical. The high stabilities of $\text{C}_6\text{H}_5\text{OO}$, $\text{OC}_6\text{H}_5\text{O}$ and $\text{C}_6\text{H}_4(\text{O})\text{OH}$ radicals strongly suggest that the major reaction channels identified for the analogous $\text{C}_2\text{H}_3 + \text{O}_2$ reactions may take place in the $\text{C}_6\text{H}_5 - \text{O}_2$ system and may account for the experimentally observed H- and O-production rates by Just and coworkers¹⁷ with the following mechanism:

where $\text{O}=(\text{C}_6\text{H}_4)=\text{O}$ represents o-benzoquinone, as given before.

Recently, we have extended the PUMP3/6-31G(d) calculation to map out the approximate PES of the $\text{C}_6\text{H}_5 - \text{O}_2$ system (see Fig. 8), emphasizing the $\text{O} + \text{C}_6\text{H}_5\text{O}$ reaction occurring at the ortho-position of the ring, for which a transition state has been found.⁵² We have computed the rate constant for the overall exothermic process:

by a multichannel RRKM calculation, $k_H = 5.5 \times 10^{-17} T^{1.38} e^{+148/T} \text{ cm}^3/\text{molecule}\cdot\text{s}$.⁵²

We plan to carry out a higher level calculation with G2M(rcc,MP2) for the $\text{C}_6\text{H}_5 + \text{O}_2$ reaction based on the key product channels identified by our $\text{C}_2\text{H}_3 + \text{O}_2$ study.⁴⁷ The new results will be employed to model the production of H, O, CO and H_2O from $\text{C}_6\text{H}_5 + \text{O}_2$ ^{17,80} and the benzene oxidation reaction for which experimental data are available.⁸⁰

C. Publications

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Table I. Absolute Rate Constants for the Reactions of C₆H₅ and C₆H₅O Studied by the CRD Method^a

Reaction	T (K)	A	B	C(K)	Reference
C ₆ H ₅ + NO	298-500	10 ^{-11.35}	0	-433	10
C ₆ H ₅ + HBr	297-523	10 ^{-10.40}	0	554	9
C ₆ H ₅ + DBr	298-500	10 ^{-10.36}	0	612	9
C ₆ H ₅ + C ₂ H ₂	297-523	10 ^{-12.43}	0	1,560	11
→C ₆ H ₅ C ₂ H+H	300-1500	9.5x10 ⁻⁴²	9.33	1,713 ^b	11
→C ₆ H ₅ C ₂ H ₂	300-1500	1.8x10 ⁻⁷	-1.63	2,711 ^b	11
C ₆ H ₅ + C ₂ H ₄	297-523	10 ^{-11.92}	0	2,250	12
→C ₆ H ₅ C ₂ H ₃ +H	300-2000	1.2x10 ⁻²²	3.50	4,200 ^b	12
→C ₆ H ₅ C ₂ H ₄	300-2000	1.5x10 ¹⁷	-9.3	6,640 ^b	12
C ₆ H ₅ + O ₂	298-473	10 ^{-11.00}	0	-161	13
C ₆ H ₅ + c-C ₅ H ₁₀	297-523	10 ^{-11.35}	0	2,039	14
C ₆ H ₅ + c-C ₆ H ₁₂	297-523	10 ^{-11.10}	0	1,913	14
C ₆ H ₅ + c-C ₇ H ₁₄	333	8.2x10 ⁻¹⁴	0		14
C ₆ H ₅ + c-C ₈ H ₁₆	333	9.010 ⁻¹⁴	0		14
C ₆ H ₅ + CCl ₄	297-523	10 ^{-11.70}	0	1,379	14
C ₆ H ₅ O + NO	297-373	10 ^{-12.12}	0	-194	15

- a. Rate constants are given by $k = AT^B \exp(-C/T)$ in units of cm³/molecule · s.
b. 1 atm pressure (Ar).

Figure Captions

1. First-order rate constant for the decomposition of $\text{C}_6\text{H}_5\text{NO}$. Circles and triangles: this work (ref. 23) at 760 torr Ar; rectangles: Horn et al., ref. 25; dashed line: Choo et al., ref. 24.
2. Rate constant for $\text{C}_6\text{H}_5 + \text{H}_2 \rightarrow \text{C}_6\text{H}_6 + \text{H}$, given in units of $\text{cm}^3/\text{molecule}\cdot\text{s}$. Open circles: this work, obtained by pyrolysis/FTIR spectrometry, ref. 32; filled circle: this work, obtained by PLP/MS; line 1, ref. 26, calculated by using our phenyl recombination rate constant; line 2, calculated by the upper limit for the reverse rate constant given by ref. 31; line 4, ref. 27, computed by their reverse rate constant; line 5, ref. 29, computed by their reverse rate constant; line 6, ref. 28, computed by their reverse rate constant; line 7, ref. 30; solid curve, this work, calculated by TST with tunneling correction, ref. 51.
3. Rate constant for the recombination of C_6H_5 radicals. Open circles: this work, ref. 39; dashed line with error limits: ref. 25; solid line: ref. 30.
4. PES of the $\text{C}_2\text{H}_3 + \text{O}_2$ reaction (this work, ref. 47).
5. PES of the $\text{CH}_3 + \text{C}_5\text{H}_5$ reaction (this work, ref. 48). The bold-faced values were calculated using G2M (rcc,MP2) and the regular ones at the B3LYP level of theory.
6. PES of the C_6H_5 system (this work, ref. 49).
7. Rate constant for $\text{H} + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_7$, given in units of $\text{cm}^3/\text{molecule}\cdot\text{s}$. Curves are the calculated values for the different pressures indicated. Dash-dotted line: ref. 76; dashed line: ref. 75; dotted line: ref. 31; +: Ackerman, Hippler, Pabgsberg, Reihs and Troe (*J. Phys. Chem.*, **94**, 5247, 1990).
8. PES of the $\text{O} + \text{C}_6\text{H}_5\text{O}$ system (this work, ref. 52). The lowest energy path for $\text{O} + \text{C}_6\text{H}_5\text{O} \rightarrow o\text{-OC}_6\text{H}_4\text{O} + \text{H}$ takes place by intermediate 2, ortho $\text{O}=(\text{C}_6\text{H}_4)(\text{O})\text{H}$, via transition state 3, $\text{O}=\text{C}_6\text{H}_4(\text{O}) \cdots \text{H}$. The identities of other TS's and intermediates can be found in ref. 52.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Profile of the potential energy surface for
the phenyl radical decomposition

Fig. 6

Fig. 7

Fig. 8