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**RATE COEFFICIENTS OF
COMBUSTION/FUEL CONVERSION REACTIONS
BY HIGH-TEMPERATURE PHOTOCHEMISTRY**

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Progress Report

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ABSTRACT

Reliable kinetic data on isolated elementary combustion reactions spanning a broad temperature range are required for modeling and scaling studies aimed at improving the performance of, and reducing the pollutant formation from, fossil-fuel burning devices. Such data are generally not available. In the present work a new technique, High Temperature Photochemistry (HTP), has been developed to provide such data. It combines the technology of the High-Temperature Fast-Flow Reactors (HTFFR) we developed to study kinetics of metal atom/oxide reactions in the 300-1900 K range with the flash photolysis technique, which although used widely for study of such combustion reactions, has previously been limited to studies at or near room temperature. This report discusses aspects of a partially complete HTP study on the reaction,

$\text{OH} + \text{C}_6\text{H}_6 \xrightarrow{(1)} \text{C}_6\text{H}_5 + \text{H}_2\text{O}$ in the 600-1300 K range, and initial work on CH_3 oxidation by O_2 and O atoms. The measurements suggest an initial value of $k_1(T) = (4.2 \pm 1.5) \times 10^{-11} \exp[-(4.0 \pm 0.7) \times 10^3/T]$, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in fair agreement with recent results obtained elsewhere in the 500-1150 K range.

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I. INTRODUCTION AND SCOPE OF WORK

The development of fossil-fuel burning devices/engines which will have more efficient fuel combustion and/or less pollutant formation than is currently possible, requires modeling and scaling studies based on reliable information concerning the kinetics of the important elementary reactions involved. Although such data are generally becoming more available and reliable, they are applicable mainly over limited temperature ranges. The goal of this program is to measure the rate coefficients of hydrocarbon reactions over a wide temperature range, e.g., from about 300 to 1900 K (100 to 3000°F), in order to overlap with both low temperature and high temperature measurement methods. There is no other technique capable of measuring at such overlapping temperature regimes; for many pertinent reactions, especially those involving free radicals, there are no measuring techniques suitable for realistic temperatures. In order to accomplish these objectives a new experimental technique, High Temperature Photochemistry (HTP), has been developed in the present work. It was achieved by merging High-Temperature Fast-Flow Reactor (HTFFR) flow tube technology developed to study the kinetics of metal atom/oxide reactions over about the 300 to 1900 K temperature range¹ with the photochemical resonance absorption/fluorescence method used in many laboratories for kinetic measurements of combustion intermediates (free radicals). The new method has been shown to provide reliable kinetic data in the 400 to 1700 K range in a study of the O/CH₄ reaction.²

II. PROGRESS

A. OH/C₆H₆ REACTION

The apparatus and procedures² have been modified. Higher intensity photolytic flashes are now obtained using a 1.0 μ F, 30 kV capacitor triggered by a 30 kV spark gap. The flash lamp fill gas is Ar flowing slowly at $\approx$ 50 Torr; the use of Ar reduces long-lived emissions from the flash lamp in the 304-306 nm (OH detection wavelengths) which arose when N₂ fill gas was used. Graphite baffles provide $\approx$ 3° collimation of the flash lamp radiation to reduce the contribution of scattered light to the signal observed at 304-306 nm.

The OH resonance lamp is a standard flow lamp,^{1,3} through which a mixture of ≈ 0.1 - 1.0% H_2O in He is flowed. A Suprasil window transmits the OH radiation while blocking vuv radiation. The detector, a bi-alkali photomultiplier tube (PMT) with a 304-306 nm narrow band interference filter, has an optional water-filled filter cell to reduce ir radiation from the hot reactor walls between it and the HTP reaction zone.

Metering of H_2O in known concentrations is accomplished by saturating part of the bath gas flow by bubbling it through distilled water at temperatures between 10 - 50°C . The saturated flow is diluted with additional dry bath gas and flowed through heated lines to achieve the desired $[\text{H}_2\text{O}]$ (ca. $1 \times 10^{15} \text{ cm}^{-3}$) in the reaction zone. C_6H_6 is metered from a high pressure reservoir of $\approx 0.01\%$ C_6H_6 in Ar prepared by injecting a known ($\approx 0.33 \mu\text{l}$) volume of liquid C_6H_6 into a 12.644 ± 0.040 l stainless steel flask and then pressurizing that flask with Ar (to ≈ 7 atm). Small flows (0.01 - $0.1 \text{ cm}^3(\text{STP})\text{s}^{-1}$) of the mixture are metered from it into the HTP reactor using a calibrated sonic orifice flow system. The entire metering system was constructed of metal, glass, and Teflon so that no organic material contacts the C_6H_6 . A uv absorption monitor of C_6H_6 reservoir concentration, consisting of a 40 cm long absorption cell with a calibrated (against a Barocel manometer C_6H_6 vapor pressure measurement) Hg 184.9 nm lamp and detector has been installed. For the 0.01% mixture, the measured absorption at 1 atm total pressure in the cell was $\approx 40\%$. This absorption monitor has been used periodically to verify the constancy of the composition of the C_6H_6 reservoir.

Measurements of $k_1(T)$ were made in the 600 - 1300 K range; the measured rate coefficients and their uncertainties are shown in Table I. Details of the measurement methods and calculation of k and σ (the standard deviation in k_1) have been discussed previously.^{1,2} The measured rate coefficient values are consistent with the $\approx 4.5 \text{ kcal mol}^{-1}$ activation energy measured in the 500 - 1150 K range by Tully et al.⁴ A linear least squares fit⁵ to the present data yields $k_1(T) = (4.2 \pm 1.5) \times 10^{-11} \exp[-(4.0 \pm 0.7) \times 10^3/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the 600 - 1300 K range. Tully et al.⁴ obtained $(2.4 \pm 0.9) \times 10^{-11} \exp[-(4.5 \pm 0.6) \times 10^3/RT]$. Thus, the present values are approximately a factor of 2-4 larger than those of Tully et al in the 600 - 1150 K region of overlap. We consider the Tully et al data to be more reliable than the data shown here because we have found the interpretation of the present data to be complicated by scattered light problems. The most serious complication is

TABLE I

HTP MEASUREMENTS OF OH + C₆H₆ RATE COEFFICIENT

T [K]	P Torr ^a	$\frac{L}{V}$ cm s ⁻¹	[Ar] 10 ¹⁷ cm ⁻³	[H ₂ O] 10 ¹⁵ cm ⁻³	[C ₆ H ₆] 10 ¹⁴ cm ⁻³	k ₁ 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹	σ s ⁻¹
584	20	20	3.3	3.0	0.3- 4.3	1.0	0.4
655	100	50	14.7	2.1	1.1-11.2	1.3	0.8
763	120	100	15.2	4.0	1.1- 4.5	2.7	0.9
858	50	50	5.6	1.1	0.5- 5.2	4.2	1.1
900	10	50	1.1	1.0	0.7- 6.3	4.5	0.6
955	170	20	17.2	0.8	0.6- 4.1	4.0	1.2
1020	200	15	18.9	2.0	0.1- 2.1	8.8	2.1
1054	20	110	1.8	1.0	0.1- 4.3	8.0	1.1
1153	50	50	4.2	0.4	0.8- 4.0	6.2	1.0
1240	20	15	1.6	0.5	0.2- 1.0	6.7	1.5
1250	170	40	13.1	0.9	0.1- 3.2	7.2	2.2
1310	25	100	1.8	0.6	0.6- 3.4	7.5	1.7

^a 1 Torr = 133.3 Pa

found to arise from detector PMT overload caused by scattered light produced from the high intensity photolysis flash. This results in the appearance of a "phantom" decay curve arising out of signals generated from the PMT while it is recovering. The OH observations are superimposed on this phantom curve, thus making it necessary to use the integration method described previously² to separate the two components. The PMT recovery curve is from 2-10 times more intense than the OH decay curve, thus making the recovery of signal more uncertain than was the case in our prior O/CH₄ study² where the integration method was highly successful.

To reduce this problem, we have installed a gating circuit to "blind" the PMT during the photolysis flash. However, further modifications are required in apparatus geometry to eliminate the problem entirely. Unlike the apparatus used in most flash photolysis/resonance fluorescence (absorption) studies, the HTP system uses a tubular geometry to allow reagents to flow through the reaction zone and minimize the times for both wall contact and exposure to high temperature. Thus, thermally unstable reactants, whose

decomposition lifetimes are larger than $\approx 10\text{-}50$ ms can be studied at high temperature. However, the geometry chosen initially, i.e., with four mutually perpendicular observation ports in the reaction zone plane results in placing the flash lamp and diagnostic lamp directly opposite one another in the fluorescence detection mode. In turn, the photolytic light scattered from the diagnostic lamp collimator and window can find its way to the detector PMT and cause the problem indicated above.

To eliminate the scattered light, a new reactor tube is being designed in which the additional ports for the diagnostic lamp radiation will be placed at 45° offset from their present locations. Thus, the flash lamp and diagnostic lamp will each face unoccupied ports which can be fitted with "light dumps." The vacuum jacket of the reactor will also be modified to accommodate the new geometry. We intend to reexamine the present data and to extend the range of the measurements when the modified apparatus is ready.

B. CH₃ OXIDATION REACTIONS

While the new apparatus is being prepared, we have initiated work on the oxidation of CH₃ by O₂ and O. The planned CH₃/O₂ and CH₃/O experiments are discussed in detail in the accompanying proposal.⁶ Initial work has centered on the feasibility of producing CH₃ by photolysis (thus far using acetone as the photolyte) and detecting it in absorption at ≈ 150 and/or ≈ 210 nm. A 1/2 m vacuum monochromator is used to isolate the detection wavelengths. A high pressure (ca. 150 Torr) Xe lamp is used to obtain the 150 nm diagnostic radiation; however, this lamp has stability problems and it was decided to use a high pressure arc lamp to detect CH₃ at 210 nm. Initial results indicate CH₃ absorption at both 150 and 210 nm (at 300 K) and work is in progress to refine and upgrade conditions to allow the study of CH₃ kinetics. It is expected that this work will occupy the remainder of the present contract year and most of the next year. When it is completed, the OH/C₆H₆ measurements will be resumed.

III. PROJECT STATUS - MANPOWER UTILIZATION AND PLANS

The project is proceeding as planned and discussed above. The Principal Investigator, Dr. Felder, has spent approximately 40% of his time on the project since the receipt of the contract. In the current contract year (1981-'82) we anticipate getting well into the measurements program on CH_3 oxidation by O and O_2 . These measurements are expected to extend into the 1982-'83 contract year and to be completed then. Experiments on formaldehyde and formyl radical reactions with O, H, and OH will then follow⁶ and extend into the 1983-'84 contract year. The additional work needed to complete the OH + C_6H_6 rate coefficient measurements will be undertaken when apparatus modifications needed for that work are completed, probably in the 1982-'83 contract year.

IV. PUBLICATIONS

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