

FINAL PERFORMANCE REPORT

for

INFRARED ABSORPTION SPECTROSCOPY AND CHEMICAL KINETICS
OF FREE RADICALS

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Principal Investigators**Introduction**

This research was directed at the detection, monitoring, and study (by infrared absorption spectroscopy) of the chemical kinetic behavior of small free radical species thought to be important intermediates in combustion. The work typically progressed from the detection and analysis of the infrared spectrum of combustion radical to the utilization of the infrared spectrum thus obtained in the investigation of chemical kinetics of the radical species. The methodology employed was infrared kinetic spectroscopy. In this technique the radical is produced by UV flash photolysis using an excimer laser and then its transient infrared absorption is observed using a single frequency cw laser as the source of the infrared probe light. When the probe laser frequency is near the center of an absorption line of the radical produced by the flash, the transient infrared absorption rises rapidly and then decays as the radical reacts with the precursor or with substances introduced for the purpose of studying the reaction kinetics or with itself. The decay times observed in these studies varied from less than one microsecond to more than one millisecond. By choosing appropriate time windows after the flash and the average infrared detector signal in a window as data channels, the infrared spectrum of the radical may be obtained. By locking the infrared probe laser to the center of the absorption line and measuring the rate of decay of the transient infrared absorption signal as the chemical composition of the gas mixture is varied, the chemical kinetics of the radical may be investigated. In what follows the systems investigated and the results obtained are outlined.

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Infrared Electronic Spectrum of C₂H

The $\tilde{A} \ ^2\Pi \leftarrow \tilde{X} \ ^2\Sigma^+$ electronic transition of C₂H and C₂D has been studied in the gas phase. One new band of C₂H of $^2\Pi \leftarrow ^2\Sigma^+$ type at 3600 cm⁻¹ has been identified and rotationally analyzed. Bands at 3856, 3729, and 3426 cm⁻¹ have been identified and assigned to C₂D. Rotational analysis of the 3856 and 3426 cm⁻¹ bands has determined that they are both of $^2\Pi \leftarrow ^2\Sigma^+$ symmetry and that in both cases the lower state is the ground state of the C₂D radical. The band at 3729 cm⁻¹ has a vibronic symmetry type $^2\Sigma^- \leftarrow ^2\Pi$ and has been assigned to a hot band of the bending mode, $\tilde{A}(0,1,0) \leftarrow \tilde{X}(0,1,0)$. All bands were least squares fitted with an effective rotational Hamiltonian. The effective structure of the linear \tilde{A} state has been determined to be $r_{CC}=1.289 \text{ \AA}$ and $r_{CH}=1.060 \text{ \AA}$.

Reaction Kinetics of C₂H

Using color center laser kinetic spectroscopy to follow the time decay of C₂H transient absorption, the rate constants for the reactions of C₂H with H₂, O₂, C₂H₂, and NO have been measured. The C₂H was produced by ArF excimer (193 nm) flash photolysis of trifluoropropyne for the H₂, O₂, and NO reactions. In the case of the C₂H₂ reaction, C₂H was produced by flash photolysis of acetylene again using the 193 nm ArF line. Excited states of C₂H which are abundant with 193 nm photolysis were relaxed by buffering the photolysis with ≈ 20 Torr of He and ≈ 160 mTorr of SF₆. Rate constants of 4.2×10^{-11} , 4.8×10^{-13} , 1.5×10^{-10} and $3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were obtained for the reactions of C₂H with O₂, H₂, C₂H₂, and NO respectively.

The mechanism of the reaction of C₂H with O₂ has been explored. There appear to be two channels producing CO product: a fast, direct one producing highly vibrationally excited CO up to $v=6$ at the same rate C₂H disappears and a slow, indirect one producing primarily ground state CO on a much longer timescale than the disappearance of C₂H. Several possible products of five direct channels were searched for and only CO was found to be produced directly although CO₂ appears to be produced indirectly in lower yield. Constraints on the mechanism of the indirect channel were described.

The rate constants for the reactions of C₂H with CH₄, C₂H₆, C₂H₄, D₂, and CO were determined by following the time decay of a C₂H infrared transient absorption line originating from the ground vibronic state using diode laser spectroscopy creating the C₂H by excimer laser flash photolysis (ArF, 193 nm) of CF₃CCH. When possible the dependence of the reaction rate on helium pressure was investigated over the range of 8-70 Torr. Second order rate constants of $3.0(2) \times 10^{-12}$, $1.3(3) \times 10^{-10}$, $3.6(2) \times 10^{-11}$, $2.3(3) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ were obtained for the reactions of C₂H with CH₄, C₂H₄, C₂H₆, and

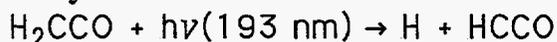
D₂ respectively. A third order rate constant of $2.1(3) \times 10^{-30} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$ was obtained for the reaction of C₂H with CO.

The rate of the reaction between C₂H and H₂ has been measured over the temperature range 295-855 K. The rate constant exhibited a non-Arrhenius form that could be well represented by the expression:

$$k = (9.44 \pm 0.50) \times 10^{-14} T^{0.9} \exp(-1003 \pm 40/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Infrared Spectrum of Ketenyl Radical (HCCO)

A new channel producing ketenyl radical (HCCO) was discovered in the flash photolysis of ketene at 193 nm.



by observation near 2020 cm^{-1} of the infrared fundamental of ketenyl corresponding to the antisymmetric motion of the heavy atoms. This band was then rotationally analyzed.

Reaction Kinetics of Ketenyl Radical

The rate constant for the reaction of ketenyl with NO has been determined to be $3.9(5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate of reaction of ketenyl radical with O₂ at room temperature has been determined as $6.5(6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and an upper bound of $1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ has been estimated for the rate of reaction of acetylene with ketenyl.

Infrared Spectrum of Propargyl Radical (H₂CCCH)

The high resolution spectrum of the ν_1 acetylenic CH stretch of propargyl radical (HCCCH₂) near 3322 cm^{-1} has been obtained and analyzed. The observed nuclear spin weights demonstrate that the CH₂ hydrogen atoms are effectively in the carbon atom plane.

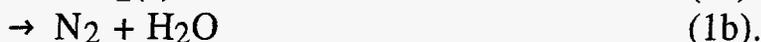
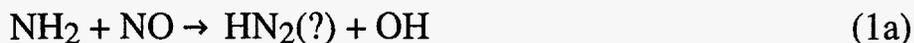
Recombination Rate of Propargyl Radical

Using the technique of infrared kinetic absorption spectroscopy, the second order rate constant for the recombination reaction of the propargyl radical (C₃H₃ + C₃H₃) has been measured and found to have the value $(1.2 \pm 0.2) \times 10^{-10} \text{ cc-molecule}^{-1} \text{ s}^{-1}$ at 295 K. The radical was produced in a flow cell by excimer laser flash photolysis ($\lambda=193 \text{ nm}$) of the precursors C₃H₃Cl or C₃H₃Br and detected using time-resolved IR absorption. Absolute concentrations of C₃H₃ were determined by comparing the C₃H₃ absorption intensity with that of the Br atom. This calibration scheme was checked by producing methyl radicals by photolysis of methyl bromide and comparing the rate constant for methyl recombination thus obtained with literature values.

The quantum yield for HCl production from the photodissociation of C_3H_3Cl at 193 nm was determined to be 0.07 ± 0.01 .

The Branching Ratio of the Thermal deNOx Reaction

Infrared kinetic spectroscopy using excimer laser flash photolysis and color center laser probing has been used to measure the branching ratio of the deNOx reaction



The branching ratio into OH of the reaction between NH_2 and NO, which is the channel thought to propagate the radical chain of the Thermal deNOx process. The amidogen radical, NH_2 , was produced by ArF photolysis of NH_3 . Infrared absorptions of OH and H_2O were measured to determine the absolute contributions of the OH and H_2O product channels. It was found that at room temperature the OH channel accounts for $13 \pm 2\%$ of the reaction. Using two different pairs of NH_3 and H_2O lines, at room temperature values of 0.85 ± 0.09 and 0.66 ± 0.03 for the ratio of H_2O formed to NH_3 photolyzed were obtained. All the H_2O signals exhibit a pronounced induction period suggesting that the H_2O is produced in very high vibrational states.

This branching ratio was then measured up to $925^\circ C$. The OH yield thus obtained is too small to maintain the process. In the $NH_2 + NO$ reaction HN_2 is thought to be formed at the same time as OH and then converted by reaction with NO to HNO. Careful monitoring of HNO infrared transition frequencies when the reactions are taking place demonstrates that HNO is not formed in this system at room temperature.

Infrared Spectrum of HCCN

The CH stretch fundamental, ν_1 , of HCCN has been observed, assigned, and analyzed. Analysis of the hot bands associated with bending shows that HCCN is a quasilinear molecule with a very floppy potential function for the HCC bending angle. The barrier to linearity is estimated to be about 200 cm^{-1} .

Rate of the Reaction $NH_2 + O$

The reaction between atomic oxygen and the amidogen radical, NH_2 , has been studied at 295 K. The room temperature rate constant for the overall reaction was measured as $(6.5 \pm 1.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The minor channel leading to $NH + OH$ was observed but accounted for at most about 8% of the NH_2 reacting. The remainder of the reaction is believed to produce the products $HNO + H$. The rate constant for the reaction $NH + O$ was determined from fitting the NH time profile to be $(6.6 \pm 1.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Infrared Spectrum of CH₂OH

The OH stretching fundamental of hydroxymethyl radical (CH₂OH) has been observed near 3600 cm⁻¹ producing the radical either by the excimer flash photolysis of acetol (CH₃COCH₂OH) or by Cl atom abstraction of a methyl hydrogen from methanol. This spectrum is extremely complex and congested presumably because there are low-lying vibrational states from the large amplitude internal rotation and inversion tunneling motions. The assignment of the spectrum to CH₂OH was confirmed by the agreement of the rate constant for the reaction of the species with O₂ with the literature value.

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