

**KINETICS AND THERMOCHEMISTRY OF POLYATOMIC FREE RADICALS:
NEW RESULTS AND NEW UNDERSTANDINGS**

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ABSTRACT

An experimental facility for the study of the chemical kinetics of polyatomic free radicals is described which consists of a heatable tubular reactor coupled to a photoionization mass spectrometer. Its use in different kinds of chemical kinetic studies is also discussed. Examples presented include studies of the $C_2H_3 + O_2$, $C_2H_3 + HCl$, $CH_3 + O$, and $CH_3 + CH_3$ reactions. The Heat of Formation of C_2H_3 was obtained from the results of the study of the $C_2H_3 + HCl$ reaction.

INTRODUCTION

Hydrocarbon photochemistry and kinetics are an integral part of the chemical processes occurring in the atmospheres of the outer planets (Jupiter and Saturn) and their larger satellites (e.g., Titan). Significant concentrations of CH_4 have been detected in these atmospheres as have lesser concentrations of higher hydrocarbons (e.g., C_2H_6 , C_2H_4 , C_2H_2 , and CH_3CCH), compounds that are produced by free-radical processes initiated by the photodecomposition of CH_4 by solar radiation.

The complex chemical processes that are responsible for producing the spectrum of hydrocarbons observed in these atmospheres involve reactions of many free-radical intermediates, some simple (such as H atoms and CH_2 radicals) and some more complex (e.g., CH_3 , C_2H_5 , and C_2H_3). To obtain a quantitative understanding of the chemical processes occurring in these atmospheres requires, among other things, knowledge of the chemical kinetics of these labile species. While there is considerable knowledge available today on the chemical kinetics of the simpler intermediates (i.e., radicals containing from 1-3 atoms), far less is known about the chemistry of the larger reaction intermediates. This dearth of knowledge for the larger species is due principally to the greater difficulty in detecting them and monitoring their behavior under controlled laboratory conditions that are suitable for obtaining quantitative information on their chemical kinetics. The powerful techniques that are available to detect atoms and small free radicals (such as laser-induced fluorescence, laser magnetic resonance, and atomic and molecular absorption) are either less sensitive, less selective, or simply not applicable for monitoring larger free radicals under the desired laboratory conditions.

Over the past several years, we have focused our attention on developing a versatile experimental facility specifically designed

for investigating the gas-phase chemical kinetics of polyatomic free radicals. It includes a heatable tubular reactor coupled to an ultrasensitive photoionization mass spectrometer.¹ Pulsed UV laser photolysis is used to produce the polyatomic free radicals of interest in the reactor. Reactants and products (stable as well as labile) are monitored in time-resolved experiments. In this paper, we describe the facility and give examples of kinetic studies of free-radical reactions which have been conducted with this facility. Some of the examples presented are elementary reactions known to be involved in the chemical transformations occurring in the atmospheres of the outer planets and their satellites.

While these examples involve exclusively hydrocarbon free radicals, it should be recognized that the versatility of this experimental facility makes it well suited for studying the kinetics of other reactions that are important in planetary atmospheres including those of radicals containing sulfur, oxygen, phosphorus, and nitrogen. Reactions involving some of these additional classes of radicals have already been conducted with earlier versions of this apparatus.²⁻⁴

THE EXPERIMENTAL FACILITY

The apparatus consists of a one-cm.-diam. quartz or Pyrex heatable tubular reactor coupled to a photoionization mass spectrometer (See Fig. 1). Gas flowing through the tube at 5 m/sec contains the free-radical precursor (e.g., acetone to produce CH_3 radicals), the molecular reactant (if a second species is also involved in the reaction under study) and the carrier gas (which is in large excess, typically 98+% He).

Pulsed homogeneous photolysis of the free-radical precursor is done with unfocused 193 or 248 nm radiation from an excimer laser (Lambda Physik 201 MSC). The laser is operated at 5 Hz to permit the gases in the reactor to be completely replaced between repetitions of the experiment.

Gas is continuously sampled through a small conical orifice (0.044-cm-diameter at the apex) located in the wall of the reactor. The emerging flow is formed into a beam by a conical skimmer before entering the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traverses the ion source, a portion is photoionized and mass selected. Photoionization is accomplished using simple yet intense atomic resonance lamps.^{5,6} The gas flowing through the lamp can be changed quickly as can the window of the lamp. The window acts as a short-wave cutoff filter to eliminate radiation from the lamp that is more energetic than the resonance radiation used for photoionization. Ionizing energies from 8.6-11.6 eV are available in about 0.5 eV steps depending on the gas flowing through the lamp. The combinations of resonance energies available for photoionization and window materials used with each lamp are shown in Figure 2. In each experiment, a photoionization energy is used, from among those available, that is as close to the ionizing energy of the free radical as possible. For example to detect CH_3 (I.P. = 9.8 eV), the hydrogen lamp is used which has a resonance energy of 10.2 eV.

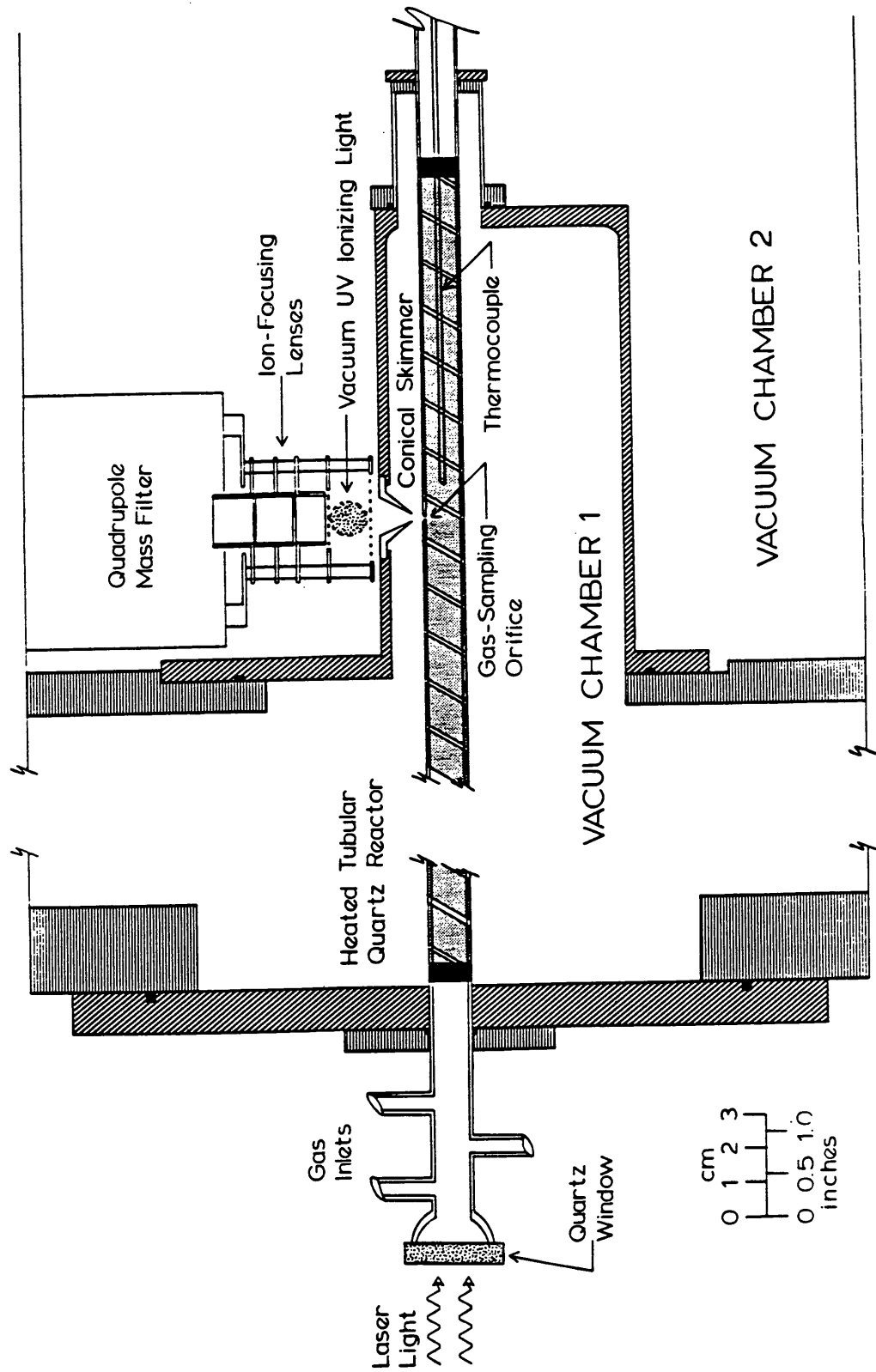


Figure 1. Drawing of Experimental Apparatus

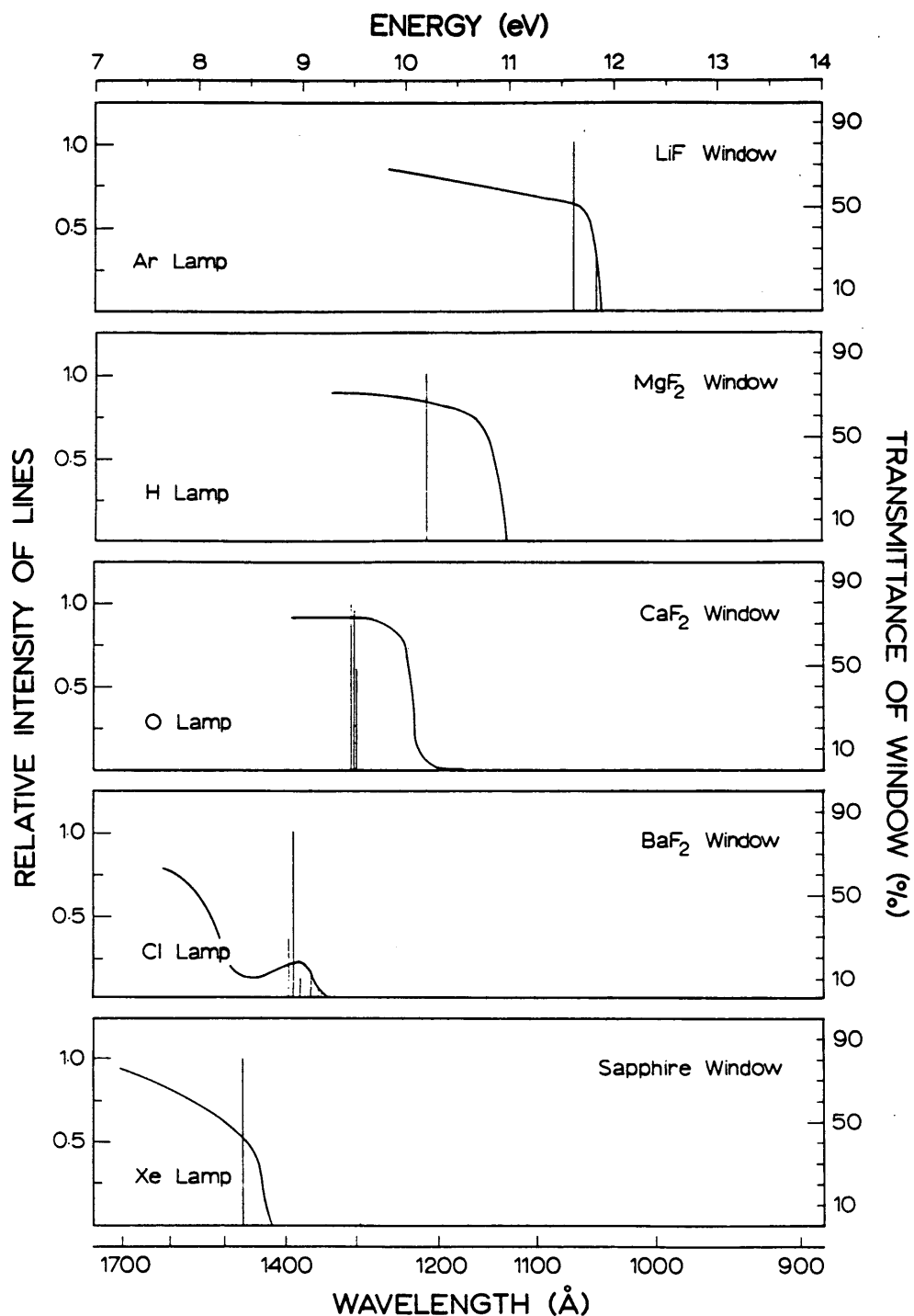


Figure 2. Characteristics of Atomic Resonance Lamps used for Photoionization. Shown are lamp gases, resonance energies, and transmission characteristics of lamp windows used with each lamp gas.

Several factors combine to give this facility unparalleled sensitivity for the detection of polyatomic free radicals. First there is the use of intense radiation from atomic resonance lamps for photoionization.^{5,6} Second, there is the high ionization selectivity that results from using essentially monoenergetic ionizing energy just above the radical's ionization potential. This practice essentially eliminates detection interference from fragmentation processes involving the free-radical precursor or the background gases in the mass spectrometer vacuum system. Third, extra sensitivity is obtained from the extreme close coupling of the reactor to the photoionization mass spectrometer in the differentially pumped vacuum system (The distance from the gas sampling point to the center of the ionizing region of the photoionization mass spectrometer is under 2 cm.). Finally, sensitivity is enhanced by using ion counting of the mass spectrometer signal and multichannel scaling, the latter to obtain time resolution and to accumulate the ion-signal profiles from repetitions of the experiment (typically 1,000-10,000).

The sensitivities of this facility for detecting polyatomic free radicals that are given below are "operational", i.e., the lowest initial free-radical concentrations that can be used in a typical experiment designed to measure free-radical decay constants. In such experiments, data acquisition is continued until the radical decay constant determinations have an uncertainty under $\pm 5\%$. Determinations of this sort that require over 30 minutes are considered impractical. Therefore, the detection sensitivities given here refer to experiments conducted for this duration.

Several factors influence the overall free-radical detection sensitivity, including photoionization cross section, degree of background interference, and the importance of heterogeneous loss of the the free radical. Because photoionization cross sections scale with the size of the free radical, detection sensitivity varies significantly, from $\approx 10^8$ radicals cm^{-3} (for larger radicals such as $(\text{CH}_3)_3\text{C}$ and SiH_3) to $\approx 10^{10}$ radicals cm^{-3} (for small radicals such as CH_3).

While the use of low-energy, nearly monochromatic, photoionization reduces fragmentation processes (sometimes totally), fragmentation occasionally is a problem and in those instances reduces effective detection sensitivity (by providing a large constant background signal). Suppression of fragmentation is excellent for most hydrocarbon radicals (where there is usually ≈ 1 eV difference between the radical ionization potential and the hydrocarbon fragmentation threshold for producing the same radical ion). Interference is significant for many nitrogen-containing compounds. This latter fact has made the technique less applicable for studies of nitrogen-centered radicals than for hydrocarbon free radicals.

First-order heterogeneous loss of the free radicals does occur at the walls of the reaction vessel. It is fully characterized through measurements of the first-order decay constant (k_w) for the radical when the second reactant is absent. However, its presence influences detection sensitivity, because reaction conditions must be used (with the second reactant present) that channel most of the

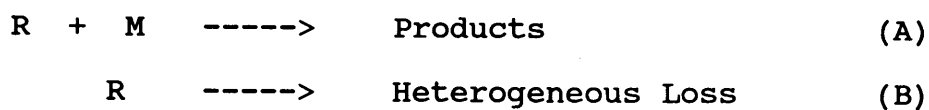
radicals through the reaction under study. In a typical set of experiments designed to determine a reaction rate constant, varying amounts of the second reactant are added to increase the radical decay constant at least a factor of 5 above k_w . It is the need to determine a set of higher decay constants under these circumstances that affects detection sensitivity. The highest wall-loss rate constant that can be tolerated is $\approx 100 \text{ s}^{-1}$ because radical decay constants can be measured accurately only up to $\approx 500 \text{ s}^{-1}$.

Reduction in detection sensitivity due to heterogeneous radical loss is inversely proportional to the wall-loss rate constant. If k_w is 100 s^{-1} , then the effective detection sensitivity is a factor of 4 lower than if $k_w = 25 \text{ s}^{-1}$. To reduce wall loss, reactor coatings are used which include boric acid, Halocarbon Wax, fluorinated Halocarbon Wax, and polytetrafluoroethylene. Recently we have begun to use a larger diameter reactor (2-cm-diameter) to lower the k_w a factor of two.

KINETIC STUDIES UNDER PSEUDO-FIRST-ORDER CONDITIONS

Radical + Molecule Reactions

The ability to use extremely low initial concentrations of polyatomic free radicals makes it possible to study their reactions with molecular species under pseudo first-order conditions, ones in which the reaction of the radical R with the molecule (M) and the heterogeneous loss of the radical are the only reactions that need be considered in the data analysis:



In these experiments, $[\text{R}]_0 \ll [\text{M}]$. The potentially important $\text{R} + \text{R}$ recombination reactions are suppressed by using initial radical concentrations below 10^{10} - 10^{11} radicals cm^{-3} . Free-radical decays are exponential under these conditions as can be seen in Figure 3 where a C_2H_3 radical decay profile is shown that was recorded during the study of the $\text{C}_2\text{H}_3 + \text{O}_2$ reaction.⁷ The rate constant for the reaction under study is obtained simply from the slope of the line through the data on a plot of decay constants vs. $[\text{M}]$.

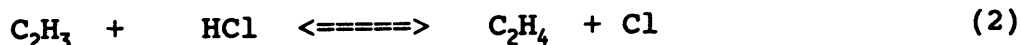
$\text{C}_2\text{H}_3 + \text{O}_2$ Reaction - In addition to rate constant determinations, the experimental facility is used to detect reaction products and hence to identify reaction channels. For example, in the case of the $\text{C}_2\text{H}_3 + \text{O}_2$ reaction, two mechanisms had been proposed prior to our investigation, one producing $\text{C}_2\text{H}_4 + \text{HO}_2$ and the other $\text{HCO} + \text{H}_2\text{CO}$. Only the latter were observed as initial products indicating that the overall reaction is



The product concentration profiles of Reaction 1 are also displayed in Figure 3. Primary processes are clearly separated from secondary ones under the conditions of these experiments. This is evident in the HCO profile in which the growth of HCO produced by reaction 1 is clearly separated from the subsequent decay of HCO due to secondary reaction of this radical with O₂. H₂CO, being a stable product, simply accumulates until the reaction is complete.

C₂H₃ + HCl Reaction - Accurate thermochemistry of polyatomic free radicals can be derived from the results of kinetic studies. When the rate constant of an elementary reaction can be measured as a function of temperature both in the forward and reverse directions, the enthalpy change of the reaction can be obtained directly from the difference in activation energies of the forward and reverse reactions.⁸

We have recently determined the heat of formation of the vinyl radical from a study of the kinetics of the equilibrium,⁹



Measurements in our laboratory of the rate constant of the forward reaction as a function of temperature yielded the Arrhenius parameters for the forward reaction. This information was combined with Arrhenius parameters for the reverse reaction obtained by Parmer and Benson¹⁰ to obtain the C₂H₃ Heat of Formation. Both Second Law calculations (using the difference in activation energies) and Third Law calculations (using values of k₁ and k₋₁ at a single temperature as well as calculated entropies of reactant and products) yielded virtually identical values for the C₂H₃ Heat of Formation, 67.1±0.6 kcal mol⁻¹ for the former and 66.9±0.3 kcal mol⁻¹ for the latter analysis. The closeness of the values using two quite different data analyses is an indication of the high accuracy of determinations of free radical Heats of Formation from the results of experiments of this kind.

Radical + Atom Reactions

Recently we have developed a procedure to study the kinetics of reactions of polyatomic radicals with atomic oxygen,
R + O.^{11,12}

It involves the simultaneous production of both reactants by 193 nm photolysis. SO₂ is the source of O:



We have investigated several R + O reactions including CH₃ + O and C₂H₅ + O,^{11,12} the former considered to have been important in the early chemistry of the Earth's atmosphere. Acetone was used as the source of CH₃,



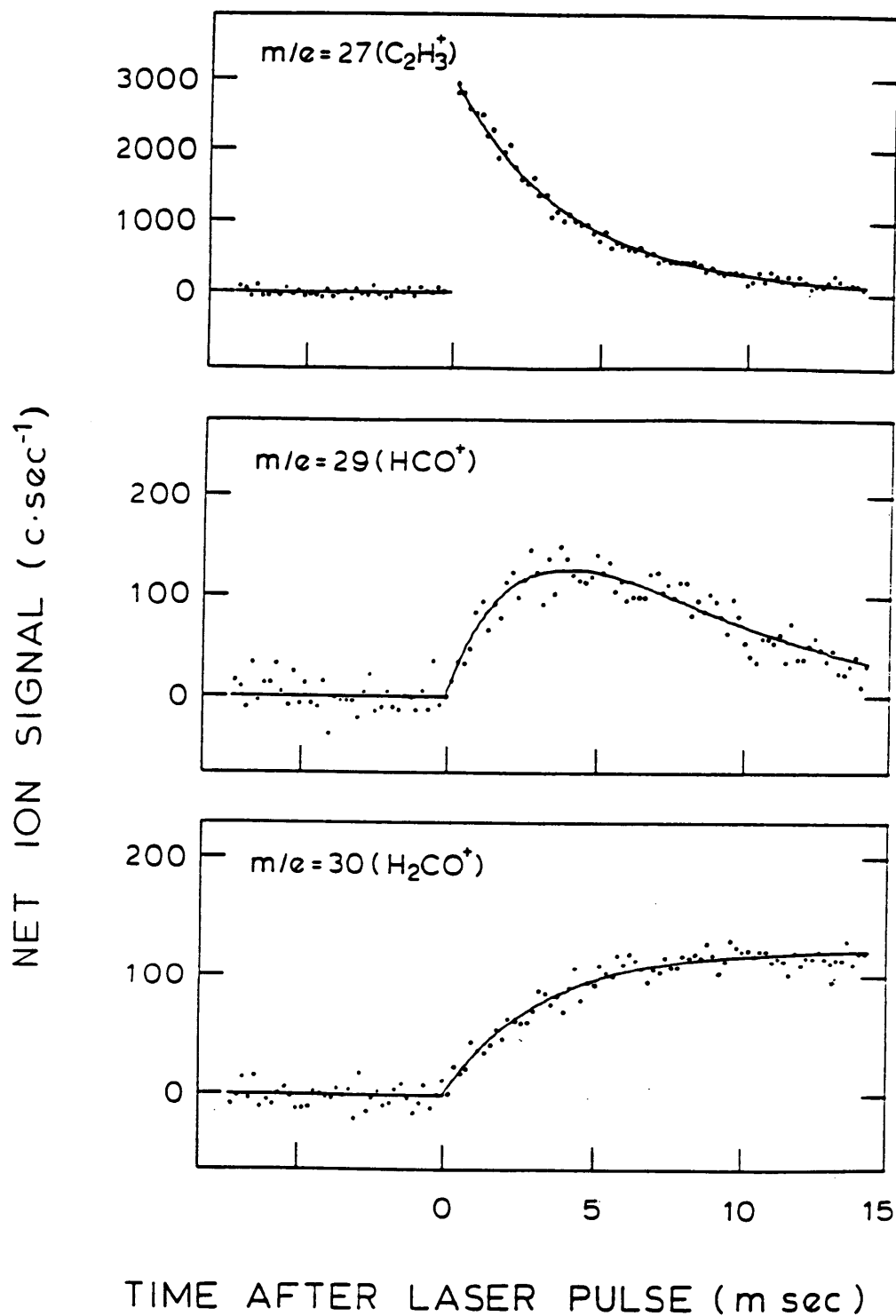


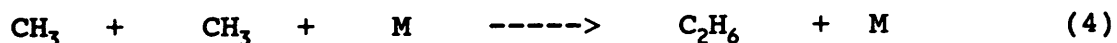
Figure 3

Plot of reactant and product ion-signal profiles recorded during $\text{C}_2\text{H}_3 + \text{O}_2 \rightarrow \text{HCO} + \text{H}_2\text{CO}$ reaction.⁷ $T=599$ K; $[\text{O}_2]=1.42 \times 10^{13}$ molecule cm^{-3}

The oxygen atoms are produced in excess and are not depleted to a significant degree during the course of the reaction. The O-atom concentration is determined by measuring the depletion of SO₂ by photolysis.

Radical + Radical Reactions

By using higher initial free radical concentrations (e.g., 10¹³ radicals cm⁻³) recombination processes can be investigated. We have studied the recombination of CH₃ radicals, ¹³ a process believed to be responsible for producing C₂H₆ in the atmospheres of the outer planets and on Titan:



In such studies, the initial concentration of the radical must be determined, and there must not be competing R + R' reactions also consuming CH₃. Again, 193 nm photolysis of acetone was used to produce CH₃. Its concentration was determined from direct observation of the depletion of acetone by the pulsed 193 nm light. Pictures of the acetone depletion and CH₃ decay profiles recorded during a set of experiments conducted to measure k₄ are shown in Figure 4.

CONCLUDING REMARKS

The apparatus described here is a versatile tool for the study of the chemical kinetics of polyatomic free radicals. It is well suited for the study of many classes of free-radical reactions. It is hoped that this introduction to the facility and its capabilities will draw attention to its potential usefulness for gaining new knowledge of the chemical processes occurring in the planetary atmospheres.

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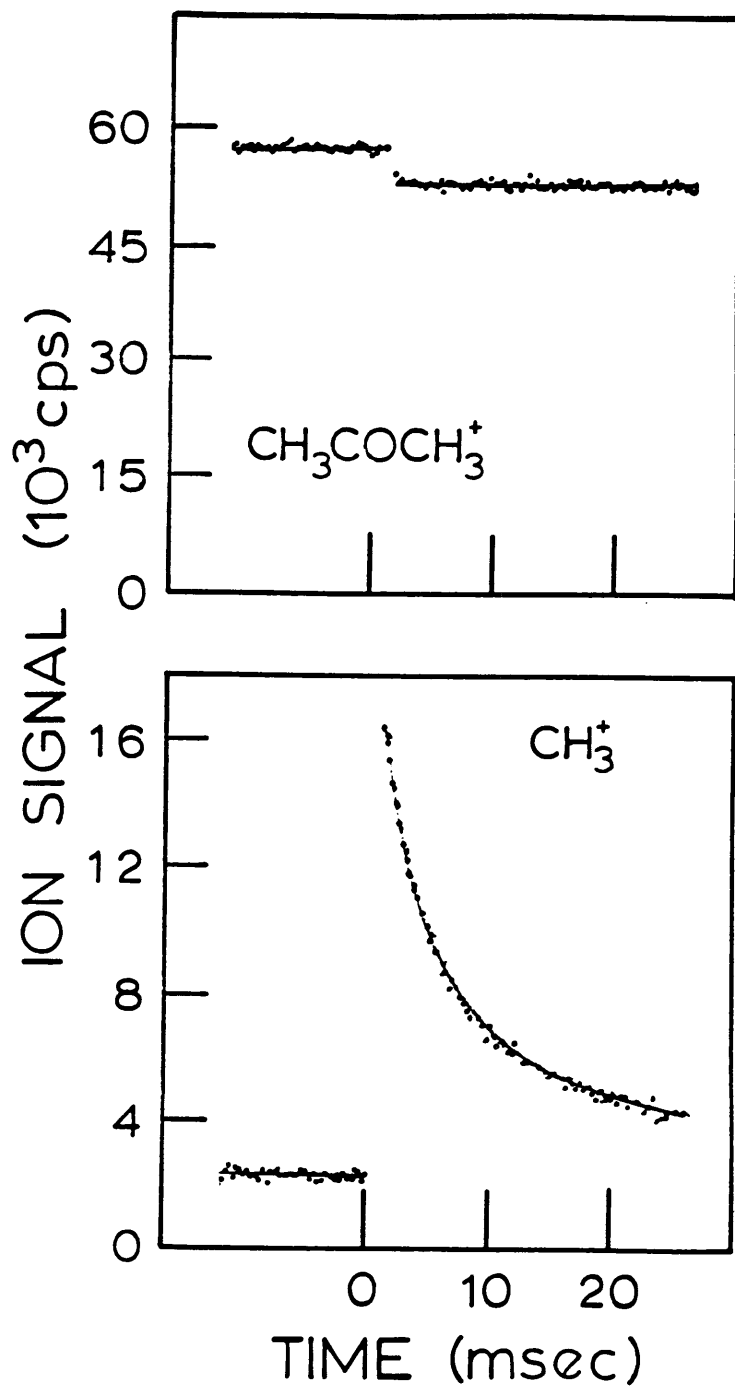


Figure 4

Plot of CH_3^+ decay recorded during $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ reaction.¹³ $T=810$ K; $[\text{CH}_3]_0=1.04 \times 10^{13}$ radicals cm^{-3} ; $[\text{He}]=2.1 \times 10^{17}$ atoms cm^{-3} .

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