

CHEMICAL KINETICS OF THE REACTION OF METHOXY WITH OXYGEN

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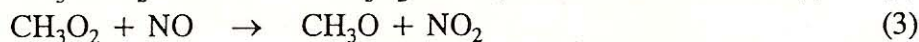
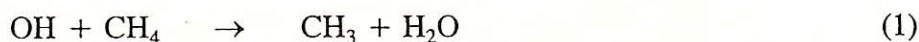
Abstract

Rate constants have been obtained as a function of temperature in the range 21.5-150.0 °C for the gas phase reaction of the methoxy (CH₃O) radical with molecular oxygen (O₂) and an appropriate Arrhenius expression $k(T) = 5.48 \times 10^{-13} \exp[-2181/T(K)]$ cm³ molecule⁻¹ s⁻¹ derived.

Introduction

Neutral free radicals are important chemical intermediates in gas-phase atmospheric and combustion phenomena.¹ Over the past few decades, our understanding of transient molecular species has been considerably enhanced by the introduction of new and novel experimental techniques, such as infrared laser absorption, microwave absorption, resonantly enhanced multiphoton ionization, and laser-induced fluorescence.² The technique of laser-induced fluorescence (LIF) has been employed to investigate the kinetics of the methoxy (CH₃O) radical. In a typical LIF experiment, methyl nitrite (CH₃ONO) molecules are photolyzed with an excimer laser (KrF @ 248 nm) to generate CH₃O fragments, which are subsequently excited from ground electronic levels to excited electronic levels by the absorption of tunable dye laser radiation. Excited CH₃O molecules can then decay back to the ground electronic level by spontaneous emission or "fluorescence".³

Methoxy (CH₃O) is produced in the troposphere as a chemical intermediate in the breakdown of methane (CH₄) by the hydroxyl (OH) radical via the following reaction sequence:⁴



The CH₃O radical generated reacts with oxygen (O₂) to produce formaldehyde (HCHO) as a stable product:⁵



The reaction of CH_3O with O_2 , resulting in HO_2 and formaldehyde (HCHO), is thought to be the major CH_3O atmospheric removal mechanism. The reaction (4) is also important in the oxidation of hydrocarbons in flames.² It is the dominant channel for the oxidation of CH_3O by O_2 . The methane oxidation sequence is important to the ozone budget and anthropogenic perturbations of it because NO is oxidized to NO_2 by both CH_3O_2 and the product radical HO_2 . This is followed by the reactions



and



In our investigations, CH_3O was generated by the photolysis of freshly synthesized CH_3ONO in a flow system with UV pulses from an excimer laser operating on the KrF transition at 248 nm. Tunable radiation produced by a Nd:YAG-pumped dye laser was frequency-doubled by a KDP crystal to generate near-UV radiation which was used for delayed probing and monitoring of the CH_3O concentration in the excited $\bar{A}^2\text{A}_1$ state via LIF. Various inert gases (e.g. helium, argon and nitrogen) were used as carriers in the flow system for transporting the CH_3ONO to the photolysis region and their effects on translationally relaxing the photofragments were studied. Chemical kinetics of the reaction of CH_3O with O_2 was investigated by probing CH_3O after a variable time delay following photolysis and initial production of the radical. The kinetic studies were performed over a range of temperatures (21.5-150 °C) and pressures (0-40 Torr) and rate constants determined for the reaction of CH_3O with O_2 .

Experimental

A schematic of the apparatus used for the kinetic studies is shown in Fig. 1. Precursors, reactants and carrier gases were introduced into the chamber through separate micrometer valves and pumped out using a mechanical pump. Carrier gases, normally helium, argon or nitrogen, serve to translationally relax the photofragments produced after photodissociation of the precursor. The methoxy (CH_3O) radical was produced by photolyzing methyl nitrite (CH_3ONO) using UV pulses at 248 nm provided by an excimer laser (Questek Impulse). The probe radiation comprised a Nd:YAG (Spectra Physics GCR-11)-pumped dye laser (Spectra Physics PDL-3) beam that was frequency-doubled using a KDP crystal incorporated within an Inrad Autotracker II. The photolysis and probe laser beams counterpropagate collinearly through the reaction cell (as illustrated in Fig. 1). Disappearance of CH_3O in the presence of O_2 was monitored by the decay of the laser-induced fluorescence (LIF) signal from the radical. Thermocouple probes were used

to monitor the temperature and a temperature-controller (Yokogawa Model UT40) utilized to maintain the temperature of the reaction zone constant. Gas flow through the cell was sufficient to insure that a fresh supply of the methyl nitrite precursor was present in the observation zone for each successive laser shot, and yet essentially static on the time scale of the reaction between methoxy and oxygen. Flow rates through the cell of the mixture of carrier gas, methylnitrite and oxygen was measured and regulated by a mass flowmeter (MKS Model 0258C) with a readout display unit (MKS Model PDR-C-1C).

The CH_3O radical concentration was probed by monitoring the fluorescence resulting from laser excitation of the A-X transition. The specific excitation wavelength used to monitor the radical was 298.0 nm (assigned $\text{A } ^2\text{A}_1 v_3'=3 - \text{X } ^2\text{E}_{3/2} v_3''=0$). For the kinetics experiments, temporal histories of the CH_3O radical were obtained by recording the LIF signal intensity as a function of increasing delay time between the photolysis and probe laser pulses. Delay between the photolysis and probe lasers was continuously swept by a boxcar averager (Stanford Research Model SR520). LIF signal from methoxy was collected at right angles to the laser beams by a 1:1 f-lens used in conjunction with a color filter (Oriel 59459) and focused onto the cathode of a photomultiplier tube (Hamamatsu R1527), and then recorded by a second boxcar averager employing a microcomputer-aided data acquisition system.

Results

The primary objective of this study was the determination of the rate constant for the reaction of CH_3O with O_2 . Sets of experiments were performed to measure the $\text{CH}_3\text{O} + \text{O}_2$ rate constant as a function of temperature in the range 21.5 -150.0 °C. At each temperature, concentration decay profiles were recorded for various O_2 pressures (0-40 Torr). An inert gas (e.g. helium, argon or nitrogen) was used as an added diluent to assure that diffusion losses of the radical from the observation volume would be constant in all experiments. LIF used for kinetic experiments was excited at 298.0 nm, since this wavelength corresponds to the strong 3_0^3 band in the excitation spectrum of CH_3O . Second-order rate constants were measured for the reaction of CH_3O with O_2 over a range of temperatures and a total pressure of 40 Torr. Quenching of the LIF from excited CH_3O by O_2 prevented the use of O_2 pressures above 40 Torr. Both the fluorescence intensity and the width of the decay curve were observed to decrease with increasing O_2 concentration. Specifically, for $T=21.5$ °C, the CH_3O radical lifetime in the reaction zone was measured to be in the range 0.8-0.3 ms corresponding to O_2 pressures in the range 0-40 Torr yielding a rate constant $k = 1.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Similar measurements yielded rate constant values 1.8×10^{-15} , 2.0×10^{-15} , 2.5×10^{-15} and $3.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for 65 °C, 70 °C, 115 °C and 150 °C, respectively. The observed LIF from CH_3O decreased significantly as the temperature was raised above 100 °C, compared to the fluorescence at room temperature.

A typical Stern-Volmer plot at $T = 21.5^{\circ}\text{C}$ of the inverse of the decay constant versus O_2 pressure is shown in Fig. 2. The slope of the line fitted through the data was used to calculate the bimolecular removal rate constants for CH_3O in the presence of O_2 at a particular temperature. The experimental uncertainty in the determination of the decay constant was $\pm 5\%$ and is indicated using error bars in the Stern-Volmer plot illustrated in Fig. 2. Similar procedures were followed to establish removal rate constant values for each temperature investigated and the following Arrhenius expression obtained for the rate constant as a function of temperature for the reaction of CH_3O with O_2 :

$$k(T) = 5.48 \times 10^{-13} \exp [-2181/T(\text{K})] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (7)$$

Three types of carrier gases were used in the kinetics investigations, namely argon, helium and nitrogen. Both the intensity of the methoxy fluorescence and the lifetime of the decay curve were obtained for all three carrier gases under identical experimental conditions. For argon as carrier, the amplitude of the fluorescence was largest and the lifetime shortest, in comparison to the corresponding values for helium and nitrogen. For example, the methoxy fluorescence lifetimes with argon, nitrogen and helium, as diluents were determined to be 180, 236 and 324 μs , respectively. Helium as carrier gas was able to quench the methoxy fluorescence more rapidly than either nitrogen or argon, while the amplitude of the fluorescence was smallest and the lifetime longest, as compared to argon and nitrogen.

Acknowledgements

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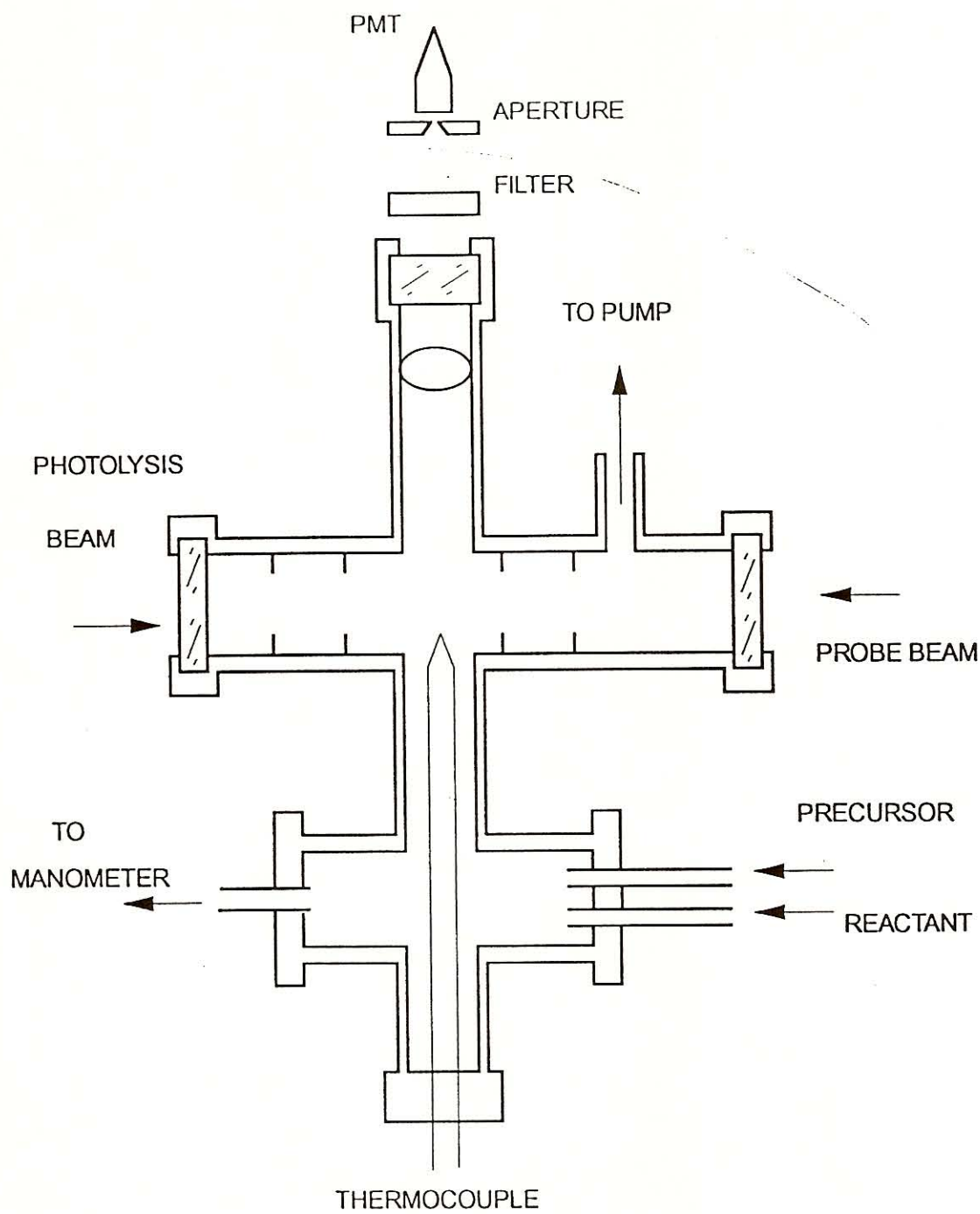


Fig. 1. Experimental arrangement for measuring CH_3O kinetics.

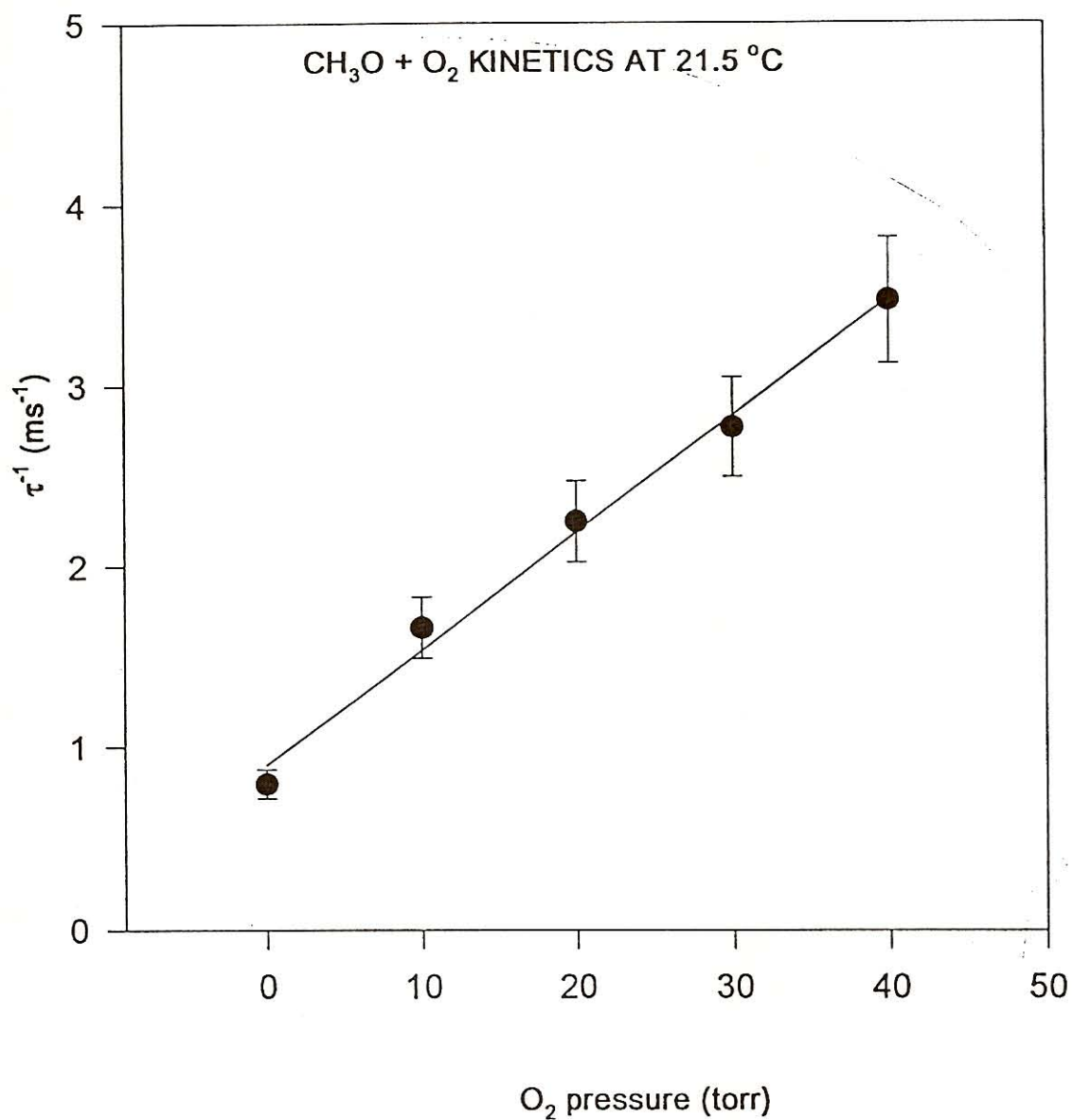


Fig. 2. Stern-Volmer plot of the inverse first-order constant (τ^{-1}) for CH₃O + O₂ reaction (at 21.5 °C) versus O₂ pressure.