LASERS '94

QUÉBEC, QUÉBEC, CANADA   DECEMBER 12–16, 1994

V.J.CORCORAN & T.A. GOLDMAN
Editors

FLUORESCENCE LIFETIMES AND KINETICS OF THE METHOXY RADICAL

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Abstract

Rate constants have been obtained as a function of temperature for the gas-phase reaction of the methoxy (CH_3O) radical with molecular oxygen. The CH_3O radical was produced by the 248 nm photolysis of methyl nitrite, and its concentration was monitored via laser-induced fluorescence. The $CH_3O + O_2$ reaction was studied in the temperature range 22 - 150 °C, and the rate constants obtained were used to derive a suitable Arrhenius expression.

Introduction

The methoxy (CH_3O) radical plays a leading role as an oxidation intermediate in the combustion of hydrocarbons and in air pollution [1,2]. Methoxy (CH_3O) is produced in the troposphere as a chemical intermediate in the breakdown of methane (CH_4) by the hydroxyl (OH) radical via the following sequence of reactions [3]: (1) $OH + CH_4 \rightarrow CH_3 + H_2O$, (2) $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$, (3) $CH_3O_2 + NO \rightarrow CH_3O + NO_2$. The CH_3O radical generated reacts with oxygen (O_2) to produce formaldehyde (HCHO) as a stable product [4]: $CH_3O + O_2 \rightarrow HCHO + HO_2$. This last reaction of methoxy with O_2, resulting in HO_2 and formaldehyde (HCHO), is thought to be the major CH_3O atmospheric removal mechanism [3]. In our laser-induced fluorescence (LIF) studies,

various inert gases (e.g helium, argon and nitrogen) were used as carriers to transport the methyl nitrite (CH_3ONO) precursor to the photolysis zone. LIF signals [5] from CH_3O, using argon as carrier, had the largest amplitude and the shortest lifetime; while helium as a buffer gas yielded the smallest amplitude and longest lifetime, and nitrogen gave a signal intermediate between argon and helium. Chemical kinetics of CH_3O with molecular oxygen (O_2) was investigated over a range of temperatures (22-150 °C) and oxygen pressures (0-40 torr), and rate constants determined.

Experimental

The kinetic experiments were conducted using a high-temperature cell . The reaction zone of the chamber was uniformly wrapped with a heating tape (Barnstead/ Thermolyne Briskheat) powered by a variable autotransformer equipped with a solid-state relay (120 V, 10A). The temperature of the reaction zone was maintained constant with a temperature-controller (Yokogawa Model UT40) and monitored with thermocouple probes (Digi-Sense JKEK Model 8528-10). Gas flow through the cell was sufficient to insure that a fresh supply of methyl nitrite precursor was present in the observation zone for each successive laser shot, and yet conditions were essentially static on the time scale of the reaction. The flow rates through the cell of a mixture of carrier gas, methylnitrite and oxygen were measured and regulated by a mass flowmeter (MKS Model 0258C) and readout (MKS Model 246). The cell pressure was monitored by an oil manometer in conjunction with a pressure sensor and gauge (Baratron MKS Model PDR-C-1C).

The CH_3O radical concentration was probed by monitoring the fluorescence resulting from laser excitation of the $A\ ^2A_1$-$X\ ^2E$ transition. The specific excitation wavelength used to monitor the CH_3O radical was 298.0 nm (assigned $A\ ^2A_1\ v_3'=3 \leftarrow X\ ^2E_{3/2}\ v_3''=0$). Laser excitation spectra of CH_3O were calibrated using optogalvanic transitions of neon [6]. For the kinetics experiments, temporal histories of the CH_3O fluorescence decay were obtained by recording the LIF signal intensity as a function of

increasing time delay between the photolysis and probe laser pulses. This delay was continuously swept by a boxcar averager (Stanford Research SR520). LIF signal from methoxy was collected at right angles to the laser beams by a 1:1 lens used in conjuction with a color filter (Oriel 59459) and focussed onto the cathode of a photomultiplier tube (Hamamatsu R1527), and then recorded by a second boxcar averager employing an IBM-compatible AT microcomputer-aided data acquisition system.

Results and Discussion

The primary objective of this study was to determine accurately the rate constant for the reaction of CH_3O with O_2. Several sets of experiments were performed to measure the rate constant of the $CH_3O + O_2$ reaction as a function of temperature. At each temperature, concentration decay profiles were recorded for various O_2 pressures (0-40 torr). The alkyl nitrite pressure was kept constant at ~20 mtorr during each set of experiments, and the decay of CH_3O was monitored over a range of reactant pressures. Quenching of the LIF of CH_3O by O_2, prevented the use of O_2 pressures above 40 torr. Fig.1 shows a typical decay curve of the LIF at 115°C from CH_3O versus the time delay between the photolysis and probe lasers. As illustrated in Fig.1., there is a decrease in the width of the curve and a decrease in the intensity of the fluorescence, as the oxygen concentration is increased. CH_3O lifetimes at different temperatures and pressures were measured and observed to decrease with oxygen pressure. Helium as buffer gas was able to quench the fluorescence more rapidly than either nitrogen or argon. Methoxy fluorescence lifetimes at 22 °C using argon, nitrogen and helium as diluents were measured to be 180, 236 and 324 μs, respectively. The observed LIF from CH_3O decreased significantly as the temperature was raised above 100 °C, compared to that at room temperature. This difficulty precluded measurements of the $CH_3O + O_2$ reaction rate constant at temperatures exceeding 150 °C.

A typical Stern-Volmer type τ^{-1} vs O_2 pressure (in torr) plot at 115 °C, where τ refers to the first-order decay constant, is shown in Fig.2. The slope of the straight line fitted through the data was used to calculate the rate constants for CH_3O in presence of O_2. Experimental uncertainty in the determination of the inverse of the first-order decay constant (τ^{-1}) was about ±5%. The rate constant, k(T=115 °C), was determined to be 2.5×10^{-15} cm^3 molecule^{-1} s^{-1}. The measured rate constants, k(T), were independent of the amount of methyl nitrite present and the intensity of the photolysis laser. The Arrhenius expression obtained for the temperature range 22-150 °C was $(6.7) \times 10^{-13}$ exp (-2277/T) cm^3 molecule^{-1} s^{-1}.

Acknowledgements

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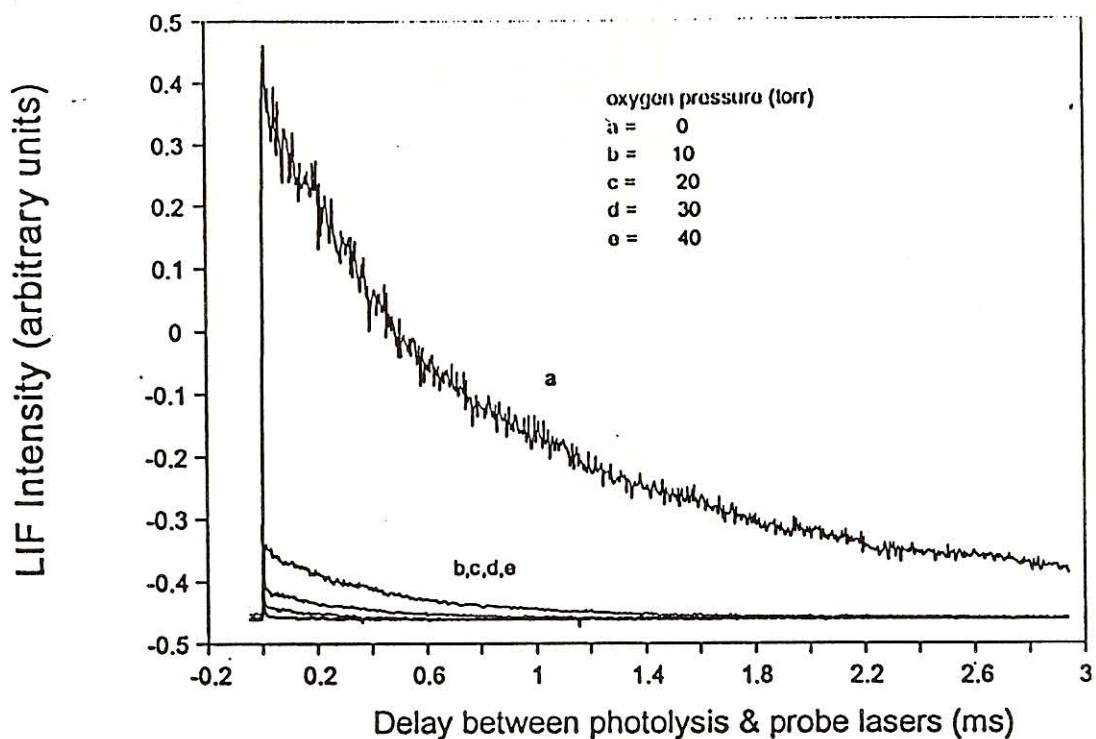6. X. Zhu, A. Nur, and P. Misra, J. Quant. Spectrosc. Radiat. Transfer, 52, 167 (1994).

Fig.1. LIF decay of the methoxy signal at 115°C for its reaction with oxygen under different pressures.
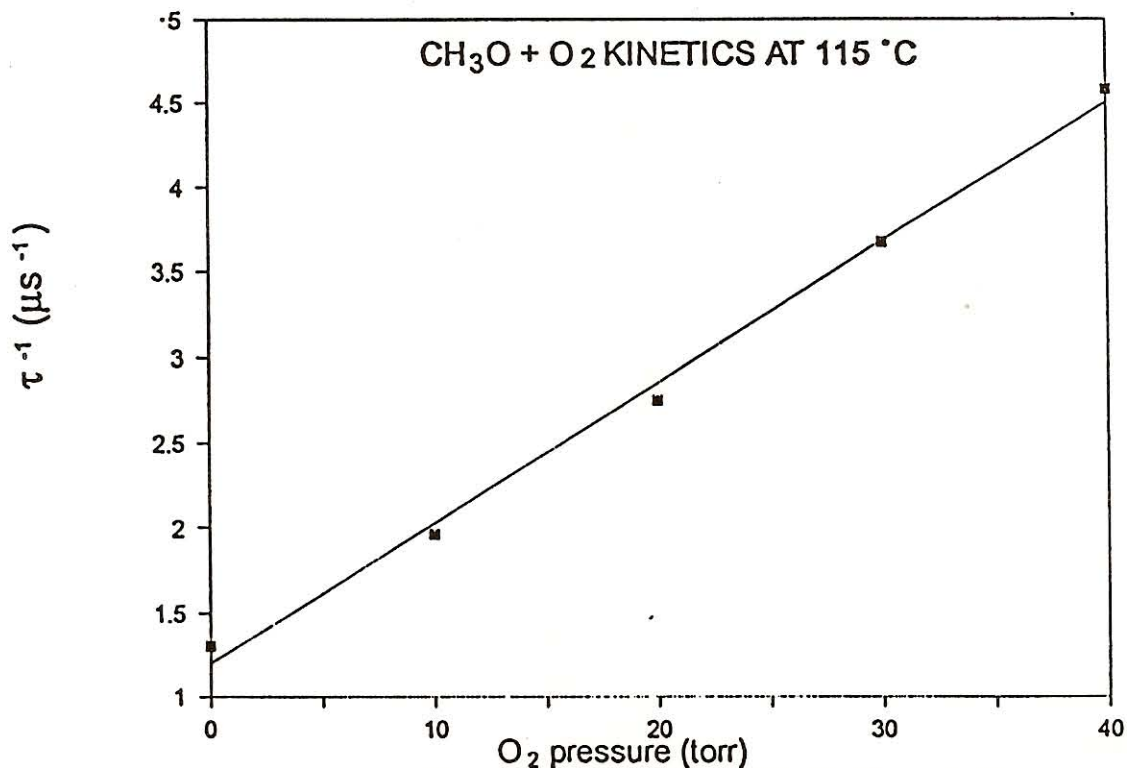

Fig.2. Stern-Volmer plot of the inverse first- order decay constant (τ^{-1}) at 115°C for the reaction of methoxy with oxygen .