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Detection of CH₂OH Radicals by Resonance-Enhanced Multiphoton Ionization Spectroscopy

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The hydroxymethyl radical, CH_2OH, has been detected by the method of resonance-enhanced multiphoton ionization mass spectrometry. Radicals were produced via hydrogen abstraction from CH_3OH by fluorine atoms in a discharge flow reactor. Tunable laser radiation between 427 and 490 nm ionized the CH_2OH radicals. The identity of the radical was determined from mass spectrometry of deuterium-substituted radicals. The isomerization reaction which transforms methoxy radicals into hydroxymethyl radicals was not observed.

Introduction

The hydroxymethyl radical, CH_2OH, appears in many reaction schemes in combustion and photochemical air pollution.[1-3] Most environments in which CH_2OH radicals participate also involve the methoxy radical isomer, CH_3O. Methoxy radicals can be detected by laser-induced fluorescence[4] allowing direct measurement of relative concentrations during kinetic studies.[5] In contrast, the hydroxymethyl radical has no previously reported electronic absorption or fluorescence spectrum. Hence, no optical diagnostic exists for CH_2OH. In this Letter we report a resonance-enhanced multiphoton ionization (REMPI) spectrum of the hydroxymethyl radical. The sensitivity and selectivity provided by these spectral features seem suitable to kinetic studies.

Experimental Section

These experiments were conducted in the laser ionization mass spectrometer described in detail in previous publications.[7,8] Only the modifications to this apparatus are discussed here. In earlier work radicals were generated by pyrolysis. In the present apparatus the pyrolysis tube was replaced by a discharge flow reactor in which hydroxymethyl radicals were produced via abstraction of hydrogen from the parent reagent by F atoms.

A schematic of the discharge flow reactor and mass spectrometer's ionizer is shown in Figure 1. The discharge flow reactor is adapted from a design by Anderson and Bauer.[9] A dilute mixture of fluorine in a helium buffer passes through a microwave discharge generating F atoms which then travel down the reactor. The CH_3OH reagent is transported down the central axis of the reactor in a small diameter tube. At the end of this tube an injector mixes the reagent with the F atoms in the reactor. The bulk of the reactants, products, and buffer gas is pumped away through an outer envelope. A small portion of the reaction products passes through a skimmer (orifice = 0.7 mm diameter) and expands into the mass spectrometer ionizer. Ions are formed at the focus of a 38-mm focal length lens, analyzed by a quadrupole mass spectrometer, and detected with a Channeltron electron multiplier.

The flow velocity of the reactor was approximately 1250 cm/s with an ambient helium pressure of 2 torr. The fluorine and methanol partial pressures were approximately 2 and 5 mtorr, respectively. Reagents used in this study were CH_3OH (ACS reagent, Aldrich Chemical Co.), CH_3OD (99.0% D, Merck and Co.), and CD_3OD (99.9% D, Merck and Co.).

The best radical yields were obtained by using an alumina tube at the microwave discharge and by coating the

walls of the reactor with halocarbon wax. Placement of the microwave discharge off-axis from the reactor greatly reduced noise pickup on the electron multiplier. Electrically grounding the vacuum fitting between the alumina tube and the reactor also suppressed noise. It was found that an excess of F atoms in the reactor's mixture induced sporadic noise bursts in the electron multiplier. Operation of the reactor with a slight excess of methanol in the mixture eliminated this problem.

The relative energy of each laser pulse was measured with an achromatic energy meter (Molectron Corp., Model J3-05) and recorded during each spectral scan. The laser dyes used for the study of F + CH_3OH were stilbene 420 (415–428 nm), coumarin 440 (427–456 nm), coumarin 460 (447–472 nm), coumarin 480 (465–500 nm), and coumarin 500 (490–530 nm). The spectrum shown in this study (Figure 2) was constructed from spectral regions of each dye where the laser energy output was relatively constant (i.e., 5 mJ/pulse). Proper relative intensities across the spectrum were maintained by comparison of band intensities in regions where the dyes overlapped.

Wavelength calibration was achieved by diverting a back reflection of the main laser beam into a neon-filled hollow cathode lamp and recording the laser-induced optogalvanic spectrum[10] during each laser scan. Wavelength corrections were then determined by comparison with tabulated neon transitions.[11]

Results

The reaction of fluorine atoms with methanol produces both hydroxymethyl and methoxy radicals:[12-14]

$$F + CH_3OH \rightarrow HF + CH_2OH \qquad (m/z\ 31) \qquad (1a)$$
$$\rightarrow HF + CH_3O \qquad (m/z\ 31) \qquad (1b)$$

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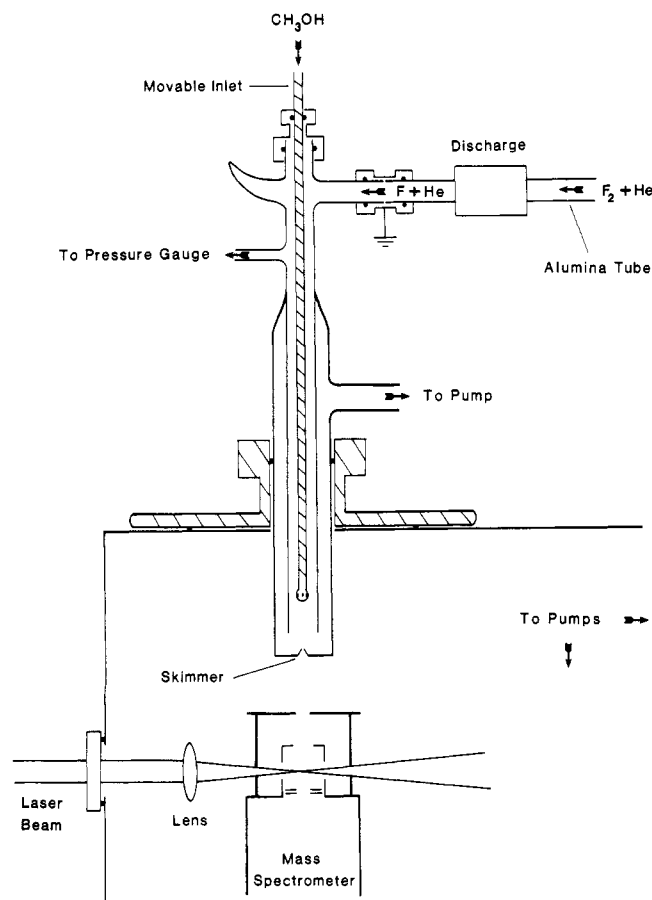
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Figure 1. Schematic of the discharge flow reactor and ionizer of the apparatus.
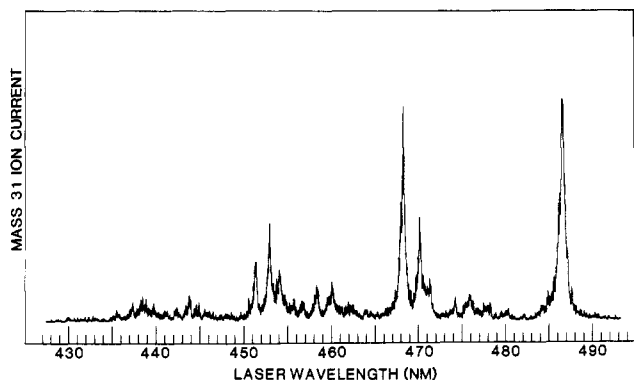

Figure 2. The mass 31 ion current as a function of dye laser wavelength (nm) induced in the discharge flow reactor effluent during the reaction, F + CH_3OH.

Bogan and co-workers have determined the product fraction of reaction 1b giving CH_3O with measurements based upon laser-induced fluorescence[15] and upon chemiluminescent chemical titration.[16] Both measurements show that CH_3O accounts for 35% of the total product.

When F atoms were allowed to react with CH_3OH in the present apparatus, the REMPI spectrum of the discharge flow reactor's effluent showed mass 31 ion signals that depended upon the concentrations of both F_2 and methanol. The signal also ceased when the microwave discharge that generated F atoms was extinguished. Figure 2 shows
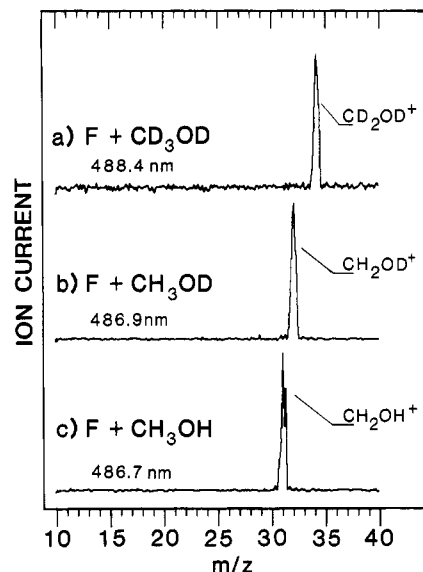
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Figure 3. The mass spectra of the discharge flow reactor effluent at the wavelength that produced maximum ion current for each reaction: (a) F + CD_3OD, 488.4 nm; (b) F + CH_3OD, 486.9 nm; (c) F + CH_3OH, 486.7 nm.

the composite spectrum of the F + CH_3OH flow reactor effluent between 427 and 493 nm. The strongest REMPI signal occurred at 486.7 nm. Other strong resonances were observed at 468.5, 470.2, and 453.0 nm. Numerous weaker REMPI resonances were also detected. Between the wavelengths 415–429 and 490–530 nm, no REMPI signals were observed.

The mass spectra of REMPI resonances observed in this study showed no fragmentation. For example, the mass spectrum of the F + CH_3OH effluent irradiated at 486.7 nm (Figure 3c) showed only mass 31 ions. In the F + CD_3OD effluent only mass 34 ions were observed (Figure 3a) and the strongest resonance shifted -71 cm^{-1} to 488.4 nm.

The REMPI signal's dependence upon the presence of F_2, CH_3OH, and the microwave discharge established that the spectrum shown in Figure 2 arose either from methoxy or hydroxymethyl radicals—or both isomers together. To determine which isomer was responsible for the spectrum, we repeated the experiments using the isotopically substituted reagent, CH_3OD. This reagent reacts with F atoms to produce isomers of different molecular weights:

$$F + CH_3OD \rightarrow HF + CH_2OD \quad (m/z\ 32) \quad (2a)$$

$$\rightarrow DF + CH_3O \quad (m/z\ 31) \quad (2b)$$

Only mass 32 ions were observed. Thus, the 487-nm bands originate only from hydroxymethyl radicals.

Additional studies showed that all REMPI signals from the effluent of F + CH_3OD originated from mass 32 ions at laser wavelengths between 429 and 500 nm. No mass 31 ion signals were observed. Thus, we conclude that all spectral features reported in the present study originate from the REMPI of hydroxymethyl radicals.

Studies of the reaction, F + CH_3OD, also provided a direct measure of the upper limit for the rate at which methoxy radicals isomerize into hydroxymethyl radicals:

$$CH_3O \xrightarrow{M} CH_2OH \quad (m/z\ 31) \quad (3)$$

Radford[17] proposed the presence of this process and determined an upper limit of 40 s^{-1} at 300 K based upon the disappearance of CH_3O as measured by laser magnetic

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resonance. In a measurement based upon CH_3O fluorescence decay, Gutman et al.[6] have estimated that isomerization at 300 K is less than 1 s^{-1}. If isomerization had been significant in the F + CH_3OD experiments described above, then a fraction of CH_3O formed in reaction 2a would have isomerized into CH_2OH and expressed itself as a mass 31 REMPI spectrum identical with Figure 2. The strength of this spectrum relative to the CH_2OD (m/z 32) spectrum would depend upon the isomerization rate, the discharge flow reactor velocity, and the branching ratio of reaction 2. If the isomerization rate were 40 s^{-1}, then in our apparatus the mass 31 REMPI spectrum would show 3% of the intensity shown by the mass 32 REMPI spectrum. We see no evidence for isomerization in our mass spectrometry studies. The noise level in our mass 31 spectra (approximately 1% of the maximum mass 32 ion signal) could conceal an isomerization rate less than 15 s^{-1}.

Discussion

The present results show the first detection of an excited electronic state of the hydroxymethyl radical. The conditions used to generate these radicals are similar to those of any flow reactor, and thus, REMPI detection of these radicals should prove useful in future kinetic studies. The absence of any ion fragmentation by the ionization process enhances sensitivity since all of the ion signal is concentrated into a single mass.

Because of the limited spectral range viewed during this study, an assignment of the resonant state's identity is premature. In fact, the present results cannot ascertain whether the electronic states that enhance the ionization cross section lie at energies that are the sum of one, two, or three protons. However, likely states involved can be speculated. The carbon atom in CH_2OH will most likely possess sp^2-hybrid bonding character with the methyl hydrogens and oxygen atom. The lone radical electron will reside in a carbon atom p orbital that is perpendicular to the methyl hydrogen–oxygen plane. In this view the bonding geometry about the carbon atom is nearly planar. Most optical transitions are characterized by the promotion of the carbon p-orbital electron into Rydberg orbitals also centered upon the carbon. Thus, like the methyl radical,[18] most of the hydroxymethyl radical electronic states are Rydberg states.

If these REMPI signals arise from resonances with a Rydberg state, possible assignments may be proposed with knowledge of the ionization potential, identification of band origins, and use of the Rydberg formula.[18] The ionization potential of CH_2OH has been measured by electron impact to be 8.1 eV.[14,19] Four 487-nm photons are required to prepare the ion. Of possible choices of Rydberg transitions, a simultaneous two-photon preparation of the 3s Rydberg state seems the most likely source of resonance enhanced ionization. Absorption of two more photons would generate the ion. The Rydberg series would possess a quantum defect of 0.87 which is reasonable for an ns Rydberg series. The assignment of the 487-nm peak to a band origin is based upon the relatively small, two-photon deuterium isotope shifts in CH_2OD (−16 cm^{-1}) and CD_2OD (−142 cm^{-1}). If this state is the 3s Rydberg state, then the detection of more members of the ns Rydberg series will confirm the assignment.

In addition to Rydberg states, the hydroxymethyl radical should also possess a single low-lying valence state that corresponds to the promotion of one electron from the sp^2 hybrid orbital to pair up with the carbon atom p-orbital electron. Since this valence state should have a pyramidal orbital geometry about the carbon atom, the Franck–Condon factors of this transition may be small unless the bonding about the carbon in CH_2OH is nonplanar in the ground state. This valence state also is a possible origin of the resonances reported in this work.

Clearly, a REMPI spectrum covering a wider spectral range than reported here is needed to enable electronic state assignments. In addition, these studies need to encompass more isotopically substituted hydroxymethyl radicals to allow assignment of the vibrational structure. These experiments are currently in progress.

Registry No. CH_3OH, 67-56-1; F, 14762-94-8; hydroxymethyl radical, 2597-43-5; methoxy radical, 2143-68-2.

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