



Surface residence time measurements of transient methyl radicals

K.A. Briggman¹, P.C. Stair^{*}, E. Weitz

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA

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Abstract

We present the first measurement of the thermal desorption kinetics of methyl radicals. Neutral methyl radicals are photochemically produced within a methyl iodide film condensed on MgO(1 0 0). A substantial fraction become trapped through inelastic collisions with the film and thermalize to the film temperature prior to desorption. Novel residence time measurements are made by comparing neutral and ion flight times in a time-of-flight spectrometer. An Arrhenius analysis of methyl radical residence times provides a desorption barrier of 2.5 ± 0.5 kcal mol⁻¹ and a pre-factor of $10^{10 \pm 1}$ s⁻¹. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Methyl radicals have been implicated as important intermediates in a variety of heterogeneous hydrocarbon reactions in connection with catalysis [1] and semiconductor thin film growth [2]. Information regarding the dynamics involved in methyl radical-surface collisions and the kinetics of subsequent competing chemisorption and desorption reactions is of primary importance in determining fundamental reaction mechanisms and predicting reaction probabilities. A microscale half-scattering experiment is described in which methyl radicals are photochemically created near a surface and allowed to interact with co-adsorbed

molecules in a thin film of methyl iodide on a MgO(1 0 0) surface. A time-of-flight detection technique measures both methyl fragment kinetic energies and surface residence time distributions. The correlation of these data allows identification of both direct desorption and trapping-desorption processes in this system. We believe these results on the nature of surface accommodation and trapping of the methyl radical have general implications for a variety of surfaces.

2. Experimental

Experiments were performed in an ultrahigh vacuum system described elsewhere [3]. Specifically, the instrument contains a single stage, time-of-flight (TOF) mass spectrometer whose flight tube is collinear with the MgO(1 0 0) surface normal. The MgO(1 0 0) surface was prepared [4] and then cooled to the appropriate temperature, monitored by a chromel–alumel thermocouple

^{*} Corresponding author. Fax: +1-847-467-1018.

E-mail address: pstair@northwestern.edu (P.C. Stair).

¹ Present address: Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA.

cemented to the side of the crystal. Room temperature CH_3I (Aldrich, >99.5%), purified by several freeze-pump-thaw cycles, was backfilled into the chamber. Previous temperature programmed desorption (TPD) studies of methyl iodide on $\text{MgO}(100)$ have shown that below 130 K CH_3I adsorbs molecularly with a constant sticking probability [5]. Both TPD analysis and photodissociation experiments suggest methyl iodide molecules pack into two- and three-dimensional clusters on oxide surfaces even at the lowest coverages. Since the experiments are insensitive to exact coverage once multilayers are achieved, and to minimize surface depletion effects, a fresh 300L CH_3I exposure was used for each experiment. This exposure condenses into multilayer (>50 ml) films on the MgO surface with the methyl iodide molecular dipoles paired in an antiparallel orientation and aligned along the surface normal [6].

A 10 Hz pulsed excimer-pumped dye laser photolysis source was frequency doubled to 257 nm which is near the maximum of the methyl iodide \tilde{A} -band. A single absorbed photon dissociates methyl iodide in <1 ps [7] to produce methyl radicals and iodine atoms. The beam was attenuated to 0.5 $\mu\text{J}/\text{pulse}$ and focused with a f20 lens onto the surface at 45° into approximately a 250 μm diameter spot. The band gap of MgO prohibits direct absorption of photons at this wavelength, avoiding any thermal or electronic excitation of the substrate. Photochemically produced methyl radicals that escape the surface and travel a distance, d (~ 5 mm), along the surface normal reach the ionization zone of the TOF spectrometer as illustrated in Fig. 1a. A second pulsed excimer-pumped dye laser, frequency doubled to 333.45 nm, selectively ionizes ground state methyl radicals via the $2+1$ resonance-enhanced multiphoton ionization (REMPI) scheme through the $3p^2A_2''$ Rydberg level [8]. The ionization beam was focused by a 10 cm focal length lens to a waist oriented along an axis perpendicular to the spectrometer flight tube and directly above the photolysis spot on the MgO surface. A programmed delay time, t_{delay} , between the firing of the two pulsed lasers selected the velocity of methyl radicals ionized according to $v = d/t_{\text{delay}}$. Since the focused laser beams have finite spatial and

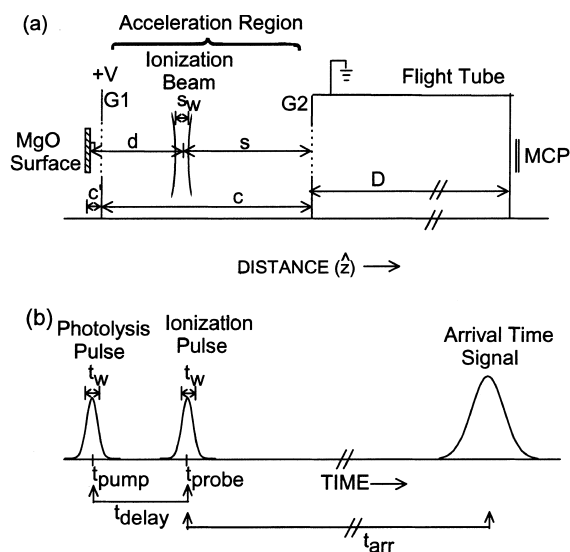


Fig. 1. Schematic showing: (a) spatial, and (b) temporal parameters of the TOF spectrometer.

temporal widths (~ 250 μm diameter beam waist and a duration of 15 ns), the velocities ionized by each combination of photolysis and ionization laser pulses have a distribution of values. The methyl ions, once formed, were immediately accelerated toward the detector by a positive voltage (+20 V) applied to grid G1 in the acceleration region of the TOF spectrometer. After crossing grid G2, the ions enter a field free region and drift toward the detector, separating in time according to their mass and initial velocity along the flight tube (\hat{z}) axis. Individual ions are detected as a function of their arrival time by a pair of multichannel plates (MCP) whose output is amplified, discriminated, and processed by a Lecroy 9450 digital oscilloscope. Data are typically summed over 5000 laser shots to obtain adequate signal-to-noise levels.

3. Results and discussion

By analyzing ion arrival times, we have previously shown [9] that the normal (\hat{z}) component of a photofragment's velocity (along the TOF axis) can be determined. The arrival time of an ion at the detector is given by:

$$t_{\text{arr}} = \frac{\sqrt{v_z^2 + 2as} - v_z}{a} + \frac{D}{\sqrt{v_z^2 + 2as}} + (t' - t_{\text{delay}}), \quad (1)$$

where v_z is the initial velocity component of the neutral particle prior to ionization, a is the acceleration due to the electric field between grids G1 and G2 defined by qE/m , s is the distance the ion travels in the acceleration region after ionization, D is the length of the field-free drift region, and the last term takes into account the difference between the programmed delay time and the precise time when ionization occurs, t' , for a particular methyl radical. For a given mass, two parameters in Eq. (1) are needed to determine a particle's arrival time, the initial velocity of the neutral particle, v_z , and the distance the ion travels in the acceleration region, s . Prior to each surface experiment, the midpoint of s is determined from a static gas phase experiment which locates the position of the ionization beam in the TOF spectrometer and monitors any drift of the beam position with time. The median of the arrival time of isotropically oriented methyl ions from the nonresonant ionization of gas phase CH_3I corresponds to an arrival time of ions formed at the midpoint of s with $v_z = 0$. Once s has been determined, the velocity of an ejected species can be directly calculated from its arrival time by solving for v_z in Eq. (1). This method of velocity measurement has been used to determine velocities from a variety of continuous sources [10].

Traditionally, velocity measurements employing pulsed photolysis sources are made by measuring the neutral flight time (delay time) of a molecule over a known distance, i.e., $v = d/t_{\text{delay}}$. This method of velocity measurement is valid provided there is **no** residence time of the molecule on the surface prior to desorption. If, however, there is a significant residence time, the delay time becomes the sum of the travel time, d/v , plus the time a particle resides on the surface, t_{surf} , after its creation. When the residence time becomes a substantial fraction of the delay time, the velocity derived from equating the delay time with the travel time is incorrect! However, if a particle's true velocity can be measured by ion arrival times,

then both the true travel time of a neutral molecule from the surface to the point of ionization and the surface residence time can be determined uniquely.

The photodissociation dynamics of methyl iodide on MgO have already been investigated with a *continuous* 257 nm photolysis source by solving Eq. (1) for v_z [11]. The velocity distribution of methyl radicals emerging from multilayer films of CH_3I has several prominent peaks: two 'fast' peaks ($v > 3000 \text{ ms}^{-1}$) with angular distributions and velocities that are associated with direct, single photon CH_3I photodissociation in concert with ground or spin orbit excited iodine followed by direct ejection into vacuum; and one 'slow' peak associated with methyl radicals slowed by collisions before leaving the film. The slow velocity peak fits a Maxwell–Boltzmann distribution with a temperature close to that measured for the surface. The slow methyl fragments also lack vibrational energy and have a broad angular distribution consistent with collisional relaxation.

Arrival time distributions of methyl ions produced by *pulsed* 257 nm photolysis of adsorbed CH_3I , followed by ionization in both the fast, Fig. 2a and slow, Fig. 2b, channels of the velocity distribution are presented for two surface temperatures, 98 and 128 K. The velocity markers on the upper and lower axes represent the nascent velocity of a neutral methyl radical assuming ionization occurs only at the midpoint of s , and at the most probable ionization time, t_{probe} . The experimental arrival time data illustrate that each delay time between the photolysis and ionization laser pulses ionizes a different velocity distribution of methyl radicals. Note that there is no shift in arrival time distribution, or associated velocities, at different surface temperatures for delay times probing in the fast velocity region. However, delay times which probe the slow ($<1200 \text{ ms}^{-1}$) velocity region exhibit a shift in arrival time with surface temperature.

A change in methyl ion arrival time reflects a change in the velocity distribution of the neutral methyl radicals. If a methyl radical resides on the surface for some time prior to departing it must have a *higher* velocity to reach the ionization zone in the same time, t_{delay} , as one which desorbs promptly. Therefore, methyl ions detected at

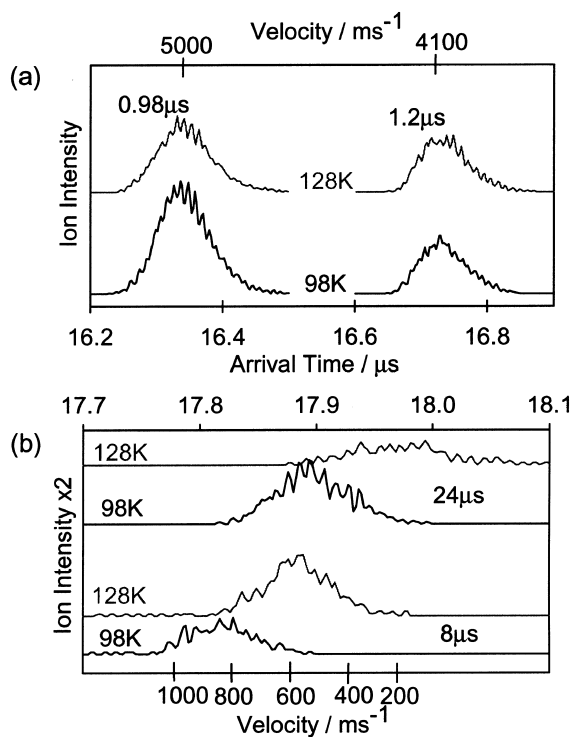


Fig. 2. Arrival time spectra of CH_3 radicals ionized in the (a) fast velocity channels at two t_{delay} , 0.98 μs and 1.2 μs ; and the (b) slow velocity channel at 8 and 24 μs . The film temperatures are 98 and 128 K as indicated in the figure.

shorter arrival times for a given t_{delay} are those which have resided on the surface for some time before desorbing. A rough estimate of the residence time can be made by inspection of the peak maxima in the arrival time distributions. For example, a t_{delay} of 24 μs will ionize methyl radicals with velocities of $\sim 200 \text{ ms}^{-1}$ if they leave the surface promptly. The maximum of the arrival time distribution at 128 K peaks at an average velocity of 200 ms^{-1} which suggests that these methyl radicals use nearly all 24 μs of the delay time to travel from the surface to the ionization point and spend little or no time on the surface following their formation. However, the arrival time maximum at 98 K peaks at an average velocity of 550 ms^{-1} , corresponding to a travel time between the surface and the point of ionization of only 9 μs . These methyl radicals must spend the remaining 15 μs of the 24 μs delay time residing on the surface prior to desorbing.

Due to the complexity of the arrival time equation surface residence times cannot be obtained directly by inversion of the measured arrival times. Surface residence times were obtained by simulation of arrival time distributions. All parameters for simulation of arrival time distributions are labeled in Fig. 1. Time and distance are referenced to the time of maximum intensity in the photolysis pulse ($t = 0$) and the position of the surface ($d = 0$). The variable for the time of creation of a particle on the surface is defined to be t_{pump} , and for the time of ionization of a neutral to be t_{probe} . The distributions associated with these variables are taken as Gaussian functions: $C(t_{\text{pump}})$ centered at $t_{\text{pumpmid}} = 0$, and $D(t_{\text{probe}})$ at t_{probemid} , each with full width half maximum (FWHM), t_w . The time an ion arrives at the detector, t_{arr} , has the distribution of Eq. (1), where t_{delay} is the constant delay time for a data set. The residence time distribution, $B(t_{\text{surf}})$ is modeled to be a first-order single exponential decay ($\exp(-kt_{\text{surf}})$) where k is desorption rate constant and the inverse of the characteristic residence time, t_{res} , and t_{surf} is the actual time a particle spends on the surface. The variables s and v_z also have distributions. The range of s is determined by the beam profile of the ionization laser whose spatial intensity distribution is also Gaussian, $A(s)$, centered at s_{mid} with FWHM, s_w . Finally, the range of velocities which are ionized is determined by the distribution of distances the neutrals can travel, divided by the distribution of times during which a neutral can be ionized, taking into account the temporal profiles of both laser beams. The actual velocities of methyl radicals ionized are given by:

$$v = \frac{c + c' - s}{t_{\text{probe}} - t_{\text{pump}} - t_{\text{surf}}}, \quad (2)$$

where c and c' are constants. The conditional probability of an ion arriving at a given time, $I(t_{\text{arr}})$, is the integrated product of the various distributions: $A(s) \cdot B(t_{\text{surf}}) \cdot C(t_{\text{pump}}) \cdot D(t_{\text{probe}})$. To simplify integration a variable, $t' = t_{\text{probe}} - t_{\text{pump}}$, is defined. Eq. (1) is then solved for t_{probe} as a function of $(s, t', t_{\text{surf}}, t_{\text{arr}})$. The change of variable from t_{probe} to t_{arr} requires a Jacobian factor $\delta t_{\text{probe}} / \delta t_{\text{arr}} = 1$. Next, substitution of the quantity, $(t' + t_{\text{pump}})$ for t_{probe} gives t_{pump} as a function of

$(s, t', t_{\text{surf}}, t_{\text{arr}})$ and another Jacobian, $\delta t_{\text{pump}}/\delta t'$. The final equation becomes:

$$I(t_{\text{arr}}) dt_{\text{arr}} = \int \int \int A(s) \cdot B(t_{\text{surf}}) \cdot C(s, t', t_{\text{surf}}, t_{\text{arr}}) \frac{dt_{\text{pump}}}{dt'} \cdot D(s, t', t_{\text{surf}}, t_{\text{arr}}) ds dt' dt_{\text{surf}} dt_{\text{arr}}. \quad (3)$$

Integration over the correct ranges of s , t' , and t_{surf} in Eq. (3) represents the selection of velocities ionized and their consequent arrival times, assuming the probability of each velocity is unity. Therefore, we introduce another multiplicative function, $v * I(v)$, into Eq. (3) prior to integration to account for the methyl radical density as a function of velocity as measured in previous studies [11]. Note that simulation of the distribution of molecules arriving in the fast velocity region, which have no measurable residence time on the surface, is simplified as $t_{\text{surf}} = 0, B(t_{\text{surf}}) = 1$. Simulations are performed analytically using Mathcad [12].

Experiments and simulations were run at four different surface temperatures, 98, 108, 118, and 128 K, and at a variety of delay times encompassing both the fast and slow velocity regions. Simulations, normalized to the raw data intensities only, are presented in Fig. 3 for the 128 K data. The peaks in the fast region were simulated with no residence time; the peaks in the slow region were simulated with both **no** residence time (thin, dashed) and a 3 μs mean residence time ($k = 1/3 \mu\text{s}$) (thin, solid). Only one set of simulation parameters was used to fit the entire data set [13]. The results of experiments and simulations at all four temperatures at a 24 μs delay time, which is most sensitive to the residence time distribution, are shown in Fig. 4. A best fit to the data for each temperature set encompassing all delay times resulted in the following characteristic residence times: 98 K, 80 μs ; 108 K, 15 μs ; 118 K, 7 μs ; 128 K, 3 μs . An Arrhenius analysis of the residence times presented in Fig. 5 provides an activation energy of $2.5 \pm 0.5 \text{ kcal/mol}$ and a pre-exponential factor of $10^{10 \pm 1} \text{ s}^{-1}$.

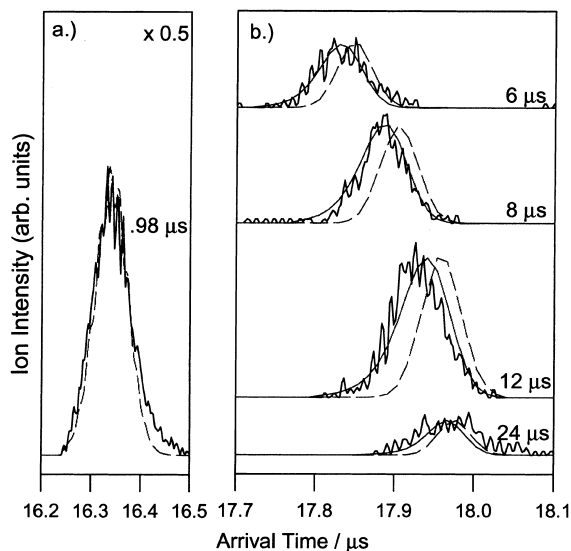


Fig. 3. Arrival time distributions for different delay times at 128 K surface temperature. Simulations are shown as curves with no residence time (dashed) and with 3 μs mean residence time (solid).

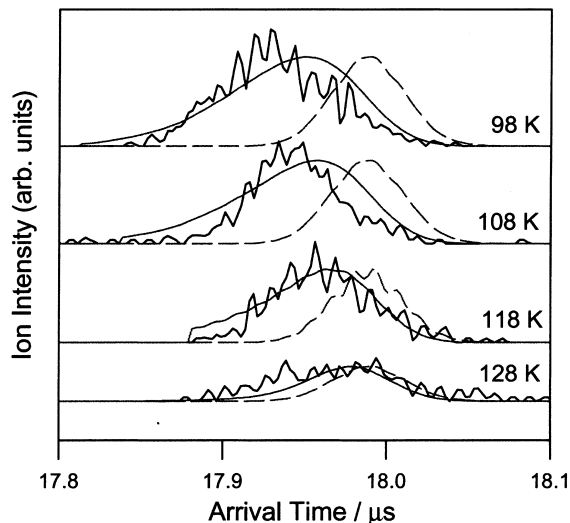


Fig. 4. Arrival time distributions for 24 μs delay time at different surface temperatures: 98, 108, 118, and 128 K. Simulations are shown as curves with no residence time (dashed) and with the following mean residence times (solid): 98 K, 80 μs ; 108 K, 15 μs ; 118 K, 7 μs ; 128 K, 3 μs .

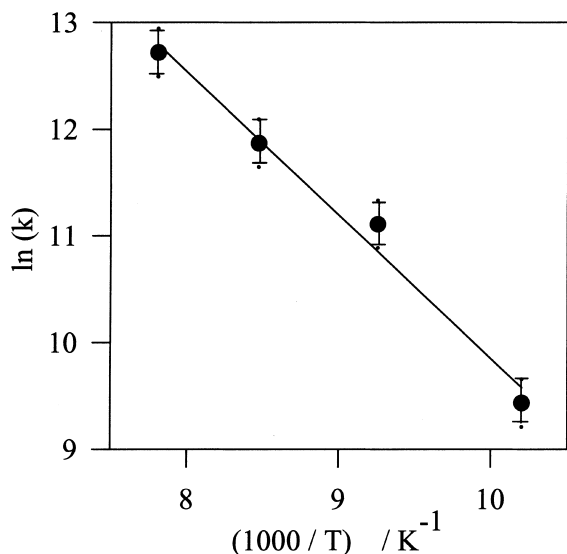


Fig. 5. Arrhenius plot of the log of the inverse residence time versus inverse temperature. The solid line is a least-squares-fit which results in an activation energy of 2.5 ± 0.5 kcal/mol and a pre-exponential factor of $10^{10 \pm 1} \text{ s}^{-1}$.

4. Conclusion

The results of the simulations are consistent with previous findings regarding the origin of methyl fragments resulting from the photolysis of methyl iodide films. Our simulations exclude residence times for the fast methyl radical velocities and support the fact that these molecules are not held on the surface for any measurable time at these surface temperatures. Additionally, the fact that only molecules with slow velocities require a finite surface residence time to describe the arrival time distributions, coupled with the Boltzmann weighting distribution used in the simulations, suggests that only those molecules which are thermalized at the film temperature become trapped on the surface for a measurable time. Since a residence time is measured only for the thermally desorbed methyl radicals, we believe the activation energy and pre-exponential characterizing this weak interaction to be of general significance. These results are on the same order as thermal desorption kinetics of related closed-shell hydrocarbon systems [14,15].

In summary, we have for the first time employed TOF arrival time information coupled with pump-probe delay times to correctly determine methyl radical residence times on a surface that are in the microsecond range. Specifically, methyl radicals are produced photochemically and allowed to interact with a methyl iodide thin film. Some molecules are trapped because they undergo inelastic scattering within the film, and quickly lose kinetic and vibrational energy until they accommodate to the surface temperature. They can spend up to tens of microseconds in this state before desorbing.

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