

Photodissociation of  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CNPh})_6$  in TetrahydrofuranXiaoliang Xie and John D. Simon<sup>\*,†</sup>Department of Chemistry, University of California at San Diego, La Jolla, California 92093  
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Picosecond absorption spectroscopy is used to examine the photodissociation of  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CNPh})_6$  (CNPh = phenyl isocyanide) in tetrahydrofuran (THF) solution. Both molecules undergo photodissociation and solvation within the time resolution of the experimental apparatus. Photolysis results in the generation of a distribution of solvation complexes, involving coordination of the alkane (CH) or oxygen moieties of the THF molecule to the vacant site on the metal. Absorption kinetics reveal the rearrangement dynamics of initially formed CH coordinated complexes to the more stable oxygen coordinated complex. The rearrangement dynamics are similar to that reported for the solvation of  $\text{Cr}(\text{CO})_5$  in alcohol solutions. The results presented disagree with a recent picosecond time resolved infrared study of the dissociation of  $\text{Cr}(\text{CO})_6$  in THF.

## Introduction

There have been several reports on the picosecond and femtosecond photodissociation dynamics of  $\text{Cr}(\text{CO})_6$  in liquids.<sup>1-7</sup> These studies reveal fast cleavage of the Cr-CO bond followed by solvent coordination to the site vacated by the photoeliminated CO. The majority of these studies have used transient absorption spectroscopy to follow the dissociation and solvent coordination dynamics. Comparison of infrared and visible absorption data from matrix isolation studies clearly shows that transient absorption spectroscopy is a powerful probe of the solvated complex,  $\text{Cr}(\text{CO})_5\text{S}$  (where S is a solvent or matrix molecule),<sup>8-11</sup> in condensed phases. The absorption band is very dependent on the solvent; in both liquids and matrices, the absorption band shifts to lower energy with decreased bonding between the chromium metal and the solvent ligand. In addition, comparison of the optical and infrared absorption spectra of solvated  $\text{Cr}(\text{CO})_5$  intermediates formed in matrices is consistent with the assignment of a  $C_{4v}$  symmetry to the complex.<sup>8</sup>

In recent papers, we have used picosecond time resolved absorption spectroscopy to examine the photodissociation of  $\text{Cr}(\text{CO})_6$  in alcohol and hydrocarbon solutions.<sup>2-4</sup> In hydrocarbon solvents, dissociation and solvation were found to occur within 1 ps. Evidence of vibrational relaxation following the coordination of a solvent molecule to the vacant site has also been observed.<sup>12</sup> In methanol, a rise time for the absorption of the  $\text{Cr}(\text{CO})_5(\text{MeOH})$  complex of 2.5 ps was reported.<sup>2</sup> This observation was interpreted in terms of the restructuring of the local solvent shell to allow formation of the solvent coordinated metal complex. This conclusion has been confirmed by femtosecond studies reported by Nelson and co-workers,<sup>7</sup> where in addition to the solvation process they have been able to resolve the dissociation event. Their studies reveal that bond breakage occurs within 250 fs of photoexcitation. In addition, evidence is reported which strongly supports the role of excited-state  $\text{Cr}(\text{CO})_5$  in the photodissociation process, in agreement with the predictions of ab initio calculations.<sup>13</sup>

In long-chain alcohols, photodissociation produces a distribution of solvent coordinated complexes. Coordination of both alkane and hydroxyl groups to the metal center has been observed.<sup>3</sup> With increasing time after photolysis, the alkane complexes rearrange to the thermodynamically more stable hydroxyl coordinated intermediate. The dynamics associated with this process are easily monitored by examining transient absorption spectra characteristic of the two molecules. Related studies in 1-propanol and 2-propanol suggest that this rearrangement process proceeds by a unimolecular mechanism.<sup>4</sup>

Recent time resolved infrared measurements of the photolysis of  $\text{Cr}(\text{CO})_6$  in THF also report the formation of a distribution of solvent coordinated complexes.<sup>6</sup> Restructuring of the alkane coordinated intermediate to the more stable oxygen-metal bond was reported to occur with a time constant  $(1/k)$  of 700 ps.

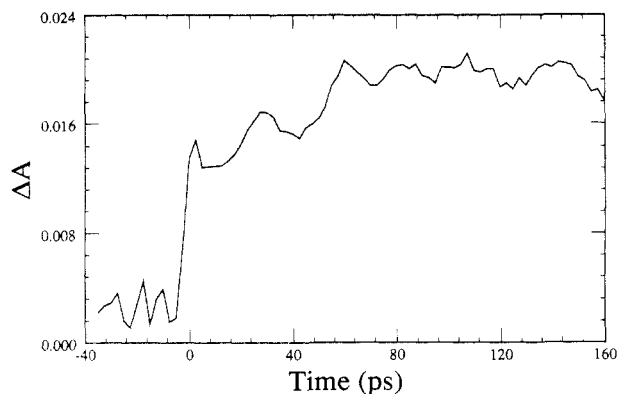
However, deconvolution of the infrared data suggested that only 5% of the complexes produced by photodissociation react by this pathway. Transient signals were also attributed to "bare"  $\text{Cr}(\text{CO})_5$ , in both  $C_{4v}$  and  $D_{3h}$  geometries. Both isomers exhibited different rates of solvation.

In this Letter, we examined the photodissociation of  $\text{Cr}(\text{CO})_6$  in THF using time resolved absorption techniques. We find that the formation of  $\text{Cr}(\text{CO})_5(\text{O}-\text{C}_4\text{H}_8)$  from initially formed  $\text{Cr}(\text{CO})_5(\text{HC}-\text{C}_3\text{H}_7\text{O})$  is complete within 200 ps. These data are consistent with observations in alcohol solution which support the conclusion that solvent coordination involves only the ground-state  $C_{4v}$   $\text{Cr}(\text{CO})_5$  isomer and occurs within a few picoseconds following dissociation.

In addition, we have carried out time resolved studies on the photodissociation of  $\text{Cr}(\text{CNPh})_6$  (CNPh = phenyl isocyanide) and the dynamics of solvent coordination to  $\text{Cr}(\text{CNPh})_5$ . To date, no picosecond time resolved studies have been performed on this system. The absorption spectrum of  $\text{Cr}(\text{CNPh})_6$  has been reported by several workers;<sup>14</sup> the complex exhibits a strong visible absorption band which has been assigned to the  $d\pi \rightarrow \pi^*$  metal to ligand charge transfer. As a result, the ground-state bleaching and recovery can easily be monitored by using picosecond absorption techniques. Such experiments have not been carried out on the hexacarbonyl system as the white light continuum which is commonly used the probe beam does not extend into the UV region where ground-state  $\text{Cr}(\text{CO})_6$  absorbs. Photolysis of  $\text{Cr}(\text{CNPh})_6$  in degassed pyridine solutions results in efficient photosubstitution of pyridine for an isocyanide ligand.<sup>14,15</sup> Various other photosubstitution reactions have been reported.<sup>16,17</sup> As observed for solvated complexes of  $\text{Cr}(\text{CO})_5$ , the solvent coordinated  $\text{Cr}(\text{CNPh})_5\text{S}$  molecule (S = pyridine, THF) absorbs at lower energies than  $\text{Cr}(\text{CNPh})_6$ ; the growth dynamics can easily be monitored at 580 nm. Thus, in addition to the ground-state

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**Figure 1.** The transient absorption signal at 440 nm is plotted as a function of time following photolysis of  $\text{Cr}(\text{CO})_6$  in THF. The data reveal an instantaneous rise at zero time followed by a slow increase in absorbance during the first 100 ps.

bleaching experiments, the formation dynamics of the solvated complex can be monitored by time resolved absorption spectroscopy.

We examine the ground-state bleaching of  $\text{Cr}(\text{CNPh})_6$  in THF and the dynamics of formation of the solvated complex,  $\text{Cr}(\text{CNPh})_5\text{THF}$ . As in the case of the hexacarbonyl, the data suggest that the  $\text{Cr}-\text{CNPh}$  bond breaks on the subpicosecond time scale and that rapid solvent coordination results in the formation of a distribution of hexacoordinate complexes involving bonding between the metal atom and the alkane and oxygen moieties of the THF molecule. The time resolved absorption data reflect the restructuring of the alkane complexes to the more stable oxygen bound system. This rearrangement process is found to be slower for  $\text{Cr}(\text{CNPh})_5(\text{CH}-\text{C}_3\text{H}_7\text{O})$  than the corresponding pentacarbonyl solvent species.

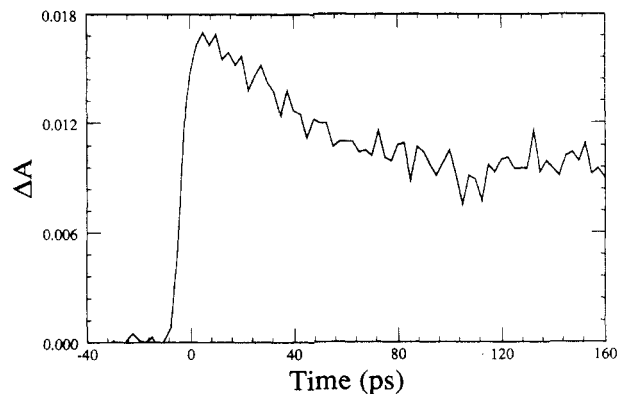
### Experimental Section

Picosecond laser pulses are generated by amplifying the output of a synchronously pumped dye laser.<sup>18</sup> The amplified pulses are  $\approx 1$  mJ/pulse,  $<1.0$ -ps fwhm, and 600 nm and occur at a repetition rate of 20 Hz. The laser output is frequency doubled to 300 nm by using a 2-mm KDP crystal providing 100  $\mu\text{J}$ /pulse. This UV light is used as the photolysis beam. The remaining red light is focused into a cell of  $\text{H}_2\text{O}$  generating a white light continuum extending from 420 to 800 nm. This light is used to record transient absorption data in a dual-beam configuration. The particular probe wavelength of interest is selected by using a narrow-band interference filter (ESCO, 5-nm fwhm). The absorption data are collected in a dual-beam configuration. The signal and reference beams are detected by large area photodiodes (DT110, EGG). The output is integrated by a sample-and-hold circuit (SRS Model 250) and digitized by a lab computer (LSI-11/23+). The delay between the pump and probe beam is achieved by means of a computer-controlled delay line (Velmex). For the data shown in Figures 1–4, approximately 200 laser shots are averaged at each delay time.

$\text{Cr}(\text{CO})_6$  was purchased from Aldrich and purified by sublimation.  $\text{Cr}(\text{CNPh})_6$  was synthesized and purified as described in the literature.<sup>15</sup> Approximately 500 mL of saturated solution was used for each experiment. The flow rate was adjusted so that fresh sample was available for each laser pulse.

### Photolysis of $\text{Cr}(\text{CO})_6$ in THF

In Figures 1 and 2, the transient absorption signals at 440 and 500 nm are plotted as a function of time following photolysis. We have previously reported that the transient absorption spectrum of the oxygen coordinated complex,  $\text{Cr}(\text{CO})_5(\text{O}-\text{C}_4\text{H}_9)$ , has a maximum at 440 nm.<sup>1</sup> Studies in hydrocarbon solvents show that the alkane complex,  $\text{Cr}(\text{CO})_5(\text{alkane})$ , has an absorption maximum in the vicinity of 500 nm. Thus, examination of the transient



**Figure 2.** The transient absorption signal at 500 nm is plotted as a function of time following the photolysis of  $\text{Cr}(\text{CO})_6$  in THF. The absorption kinetics reveals an instrument response limited rise followed by a decay of 50% of the signal within 100 ps.

signals at 440 and 500 nm enables us to determine both the distribution of alkane and oxygen coordinated complexes formed immediately after photolysis as well as the kinetics of the thermal rearrangement of initially formed alkane complexes to the thermodynamically more stable oxygen coordinated species.

The dynamics at 440 nm reveal a pulse width limited rise followed by an increase in signal during the following 100 ps. For time delays between 100 ps and 3 ns, no change in signal is observed.<sup>19</sup> This behavior is consistent with previous observations in alcohol solutions. The instantaneous rise corresponds to solvent coordinated intermediates formed immediately after photodissociation. The increase in absorption observed at 440 nm between  $t = 0$  and  $t = 150$  ps following photolysis reflects the unimolecular rearrangement of the solvent coordination from a CH to an O-bonded complex. This is supported by the data observed at 500 nm. Following an instrument response limited rise, the transient absorption decreases. The increase in transient absorption at 440 nm and the decrease in signal probing at 500 nm occur on the same time scale, supporting the conclusion that the two wavelengths are monitoring a simple kinetic process, the migration of the solvent bond from CH coordination to O coordination.

These observed dynamics are very similar to that observed in short-chain alcohol solutions. Assuming that photolysis results in a random distribution of solvent coordinated fragment, the structure of THF suggests that the solvent rearrangement process would be characterized by a rate between that observed in ethanol and propanol solutions. This is what is observed. This consistency between dynamics observed in THF and alcohol solutions strongly supports the conclusion that transient absorption data are sensitive to the different solvent coordinated intermediates and that the thermal rearrangement of the initially formed distribution to the stable oxygen coordinated molecule can be determined from the time dependence of the transient absorption signals.

The above data are contrasted to a recent infrared study reported by Wang et al.<sup>6</sup> In that study, a kinetic fit to transient infrared signals suggested that the rate of THF migration from CH attachment to O coordination occurred with a rate constant of 700  $\text{ps}^{-1}$ . Furthermore, the infrared data suggest that only  $\approx 5\%$  of the pentacarbonyl molecules produced coordinate to a CH group of the solvent. These conclusions are not consistent with the transient absorption data. The time resolved absorption at 440 nm (the absorption peak of the  $\text{Cr}(\text{CO})_5(\text{O}-\text{C}_4\text{H}_9)$  complex) does not reveal any time evolution for delay times longer than 100 ps, clearly showing that the rearrangement process must be complete on the tens of picosecond time scale. This is supported by the transient data observed probing at 500 nm. This time scale of solvent migration is at least an order of magnitude faster than that inferred from the transient infrared study. Furthermore, if we assume that the extinction coefficients of the alkane and oxygen

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coordinate complexes are similar,<sup>20</sup> the initial distribution can be evaluated from the magnitude of the absorption signal at  $t = 0$ . The data shown in Figures 1 and 2 give the results that  $\approx 80\%$  of the chromium complexes coordinate to a CH moiety of the solvent immediately following photodissociation. This is consistent with the idea of random coordination of the  $\text{Cr}(\text{CO})_5$  fragment to any available solvent site, in agreement with the interpretation of similar data in alcohol solutions.

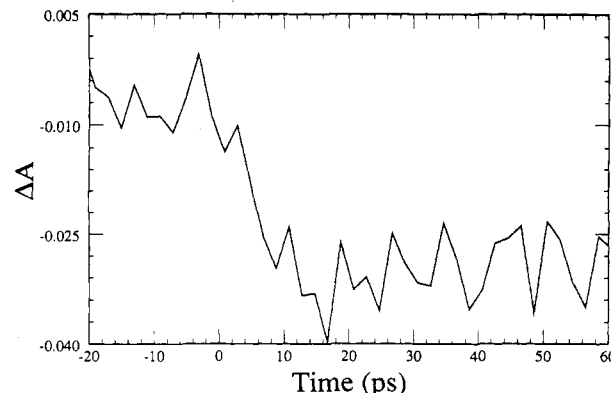
Wang et al. claim that simulation of absorption spectra of the intermediates and products can create transient absorption signals which do not reflect solvent reaction rates.<sup>6</sup> However, it must be stressed that transient absorption studies in matrices and solution show a correlation between the chromium-solvent bonding and the optical absorption spectrum. Matrix work (involving measurement of both optical and infrared data) clearly shows that if a bare " $\text{Cr}(\text{CO})_5$ " fragment were to exist, the electronic absorption spectrum would be in the region of 650 nm. Such a conclusion is supported by transient absorption studies in the nonbonding solvent perfluoromethylcyclohexane. In this system, Kelley and Bonneau report that the solvent coordinated complex absorbs at 620 nm, similar to that observed in neon matrices.<sup>21</sup> The absorption band tails off by 500 nm, showing that studies at the wavelengths reported in this paper would not measure the bare complex. Furthermore, if the  $C_{4v}$  and  $D_{3h}$  isomers of  $\text{Cr}(\text{CO})_5$  and the solvated products were to have overlapping absorptions, the lack of any change in the intensity of our transient absorption signals throughout the region of 500–550 nm for the photolysis in cyclohexane would argue that all intermediates have identical spectral properties (shape and oscillator strength) in this region. This conclusion is not consistent with the large body of absorption data that have been published. It is possible that the intense 266-nm pump beam used in the transient infrared study could result in multiphoton processes leading to a variety of coordinatively unsaturated species, and the dynamics observed may not involve the pentacarbonyl species. The intensity of the 300-nm pump beam used in our studies is approximately 2 orders of magnitude weaker than that used in the IR study.

Further support that the transient absorption data for  $\text{Cr}(\text{CO})_6$  are reflecting the dissociation and solvation process can be obtained from related studies on the visibly absorbing  $\text{Cr}(\text{CNPh})_6$  complex.

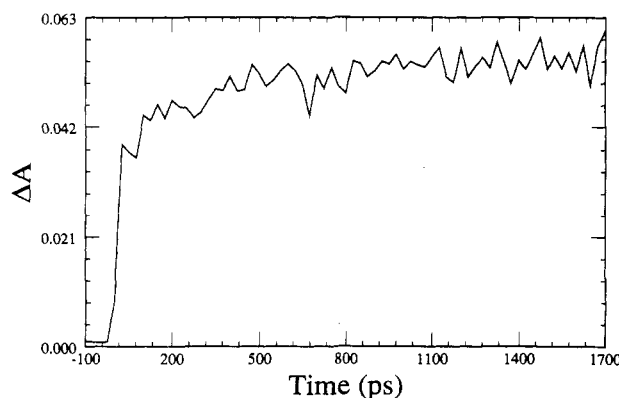
### Photolysis of $\text{Cr}(\text{CNPh})_6$ in THF

The ground-state absorption spectrum of  $\text{Cr}(\text{CNPh})_6$  has been reported by Gray and co-workers.<sup>14,15</sup> The absorption spectrum is characterized by several bands in the visible region of the spectrum which have been assigned to metal to ligand charge-transfer transitions. These states are dissociative and result in the cleavage of a single metal-CNPh bond. The dissociative nature of the excited state is confirmed by the absence of emission in these complexes; however, emission is observed from the related Mo and W systems.<sup>14</sup> Photolysis in pyridine clearly shows the formation of  $\text{Cr}(\text{CNPh})_5(\text{pyridine})$ ; this molecule is also characterized by visible absorption bands. The bands are shifted to lower energy, consistent with observation in photodissociation and solvent coordination reactions of  $\text{Cr}(\text{CO})_6$ . Although the solvent coordinated complexes of  $\text{Cr}(\text{CNPh})_5$  have not been isolated, the species giving rise to the new visible absorption has also been characterized by infrared spectroscopy; the data are consistent with a  $C_{4v}$   $\text{Cr}(\text{CNPh})_5\text{S}$  complex.<sup>22</sup>

In order to examine the possible contribution of geminate recombination following photodissociation, transient absorption data were collected probing at 460 nm. The result is shown in Figure 3. This wavelength corresponds to the ground-state absorption of  $\text{Cr}(\text{CNPh})_6$ . Ligand substitution reactions have clearly shown a decrease in absorption at this wavelength with product formation, suggesting that there is minimal overlap between the absorption



**Figure 3.** The ground-state bleaching of  $\text{Cr}(\text{CNPh})_6$  in THF is examined by plotting the time dependence of the absorption at 460 nm. The data reveal a pulse width limited bleach followed by a constant signal. No evidence for repopulation of ground-state  $\text{Cr}(\text{CNPh})_6$  is indicated for delays up to 3 ns following excitation.



**Figure 4.** The growth of the  $\text{Cr}(\text{CNPh})_5(\text{THF})$  complex is examined by monitoring the time-dependent absorption signal at 580 nm. The transient signal shows two components. The majority of the signal rises ( $\approx 70\%$ ) within the instrument response, indicating rapid dissociation and solvent coordination. The slow component observed during the first 600 ps following photolysis is interpreted in terms of the restructuring of photogenerated alkane coordinated complexes to the more stable oxygen coordinated molecule.

bands of the parent hexaisocyanide complex and the solvated intermediate. Upon photoexcitation, a bleaching is observed. The kinetics of the decrease in absorbance is pulse width limited, and no change is observed for delay times up to 3 ns following photolysis.

The buildup of the product  $\text{Cr}(\text{CNPh})_5\text{THF}$  can be determined by monitoring the transient absorption signal at 580 nm. Data obtained at this probe wavelength are shown in Figure 4. The time resolved signal reveals an instantaneous rise in absorption followed by a slow increase in magnitude for the following 600 ps. For time delays longer than 600 ps, no change is observed. The initial pulse width limited rise accounts for  $\approx 70\%$  of the total transient signal observed on the nanosecond time scale.

The instantaneous rise in the transient absorption signal at 580 nm indicates that a significant concentration of the solvated complex is formed within the instrument response. Combined with the bleaching dynamics at 460 nm, it can be concluded that dissociation from the excited state of  $\text{Cr}(\text{CNPh})_6$  is rapid (sub-picosecond) and that there is no geminate recombination on the hundreds of picosecond time scale. The two-component rise of the transient signal at 580 nm is similar to that observed at 440 nm for the related photolysis of  $\text{Cr}(\text{CO})_6$ . This similarity suggests that the increase in the transient signal at 580 nm with increasing delay time reflects solvent migration from an initially formed alkane complex to the more stable oxygen coordinated species. Unfortunately, we were unable to resolve the time-dependent signal from an alkane complex. The spectrum of an alkane coordinated complex has not been reported. However, comparison with the hexacarbonyl system suggests that the complex absorbs in the

(20) Irradiation of identical concentrations of  $\text{Cr}(\text{CO})_6$  in THF and cyclohexane was used to determine the relative extinction coefficients of the two complexes at the wavelengths of interest.

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near-infrared region of the spectrum, not within the wavelength range which we can currently probe (400–700 nm). It is interesting to note that the time scale associated with the restructuring of  $\text{CrL}_5(\text{CH}-\text{C}_3\text{H}_7\text{O})$  to  $\text{CrL}_5(\text{O}-\text{C}_4\text{H}_8)$  ( $\text{L} = \text{CNPh}, \text{CO}$ ) is approximately 4 times longer in the case of the phenyl isocyanide complex. This difference in kinetics could be accounted for by changes in the metal-solvent bond strengths as well as steric considerations in the isocyanide complex.

The transient absorption data for  $\text{Cr}(\text{CNPh})_6$  show that excitation results in efficient bond cleavage followed by rapid solvent

coordination. These results are in agreement with the conclusion of optical studies of  $\text{Cr}(\text{CO})_6$ . In both molecules, evidence for the formation of a distribution of solvated complexes is observed. The time dependence of the absorption signal reveals the relaxation of silane coordinated complexes to the more stable oxygen coordinated intermediate.

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## Kinetics of the Methoxy Radical Decomposition Reaction: Theory and Experiment

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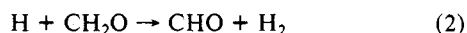
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The rate constant for the unimolecular decomposition of the methoxy radical,  $\text{CH}_3\text{O} + \text{M} \rightarrow \text{CH}_2\text{O} + \text{H} + \text{M}$ , is determined both theoretically and experimentally. In the theoretical calculations, potential energy surface information is obtained from ab initio multiconfiguration SCF and multireference configuration interaction calculations using basis sets of up to triple- $\zeta$  plus polarization quality. The zero point corrected forward and reverse barriers are calculated to be 25.6 and 8.0 kcal/mol, respectively. RRKM rate calculations are performed incorporating a quantum correction due to tunneling through an Eckart barrier fit to represent the MRCI/TZP energetics and the shape of the MC-SCF/DZP vibrationally adiabatic potential energy curve in the saddle point region. The calculated values compare closely with experimental data derived from kinetic modeling of CO formation rates measured in the thermal decomposition of methyl nitrite at 550–700 K in a static cell and at 1060–1620 K in shock waves.

### Introduction

The methoxy radical is one of the most important and ubiquitous combustion intermediates; it is known to be present in almost all hydrocarbon and many other organic compound combustion reactions. The rapid breakdown of large alkyl groups at high temperatures ultimately gives rise to the smallest and most stable alkyl radical,  $\text{CH}_3$ , which can be readily oxidized to  $\text{CH}_3\text{O}$  by  $\text{O}_2$ ,  $\text{OH}$ , and  $\text{HO}_2$ .<sup>1</sup>

The unimolecular decomposition of  $\text{CH}_3\text{O}$  produces a hydrogen atom and a formaldehyde molecule, providing the following important chain processes at high temperatures:



These rapid chain reactions also prevent kineticists from directly and reliably determining the values of  $k_1$ , the rate constant for the unimolecular decomposition of the  $\text{CH}_3\text{O}$  radical.

All of the values of  $k_1$  used in the literature for numerical modeling of combustion processes are derived either from indirect modeling involving complex chemistry or from theoretical calculations based on estimated thermochemical data.<sup>2,3</sup> To our knowledge, there have been no accurate kinetic data on reaction 1 in the literature that derive from direct rate measurements. Since neither the forward nor the reverse barrier of reaction 1 has been experimentally determined, theoretically predicted values using statistical unimolecular reaction rate theories (such as RRK or RRKM)<sup>2,4</sup> are not expected to be very reliable. The problem

becomes worse if the reverse barrier is large, wherein tunneling effect may be significant.

In this study, we have experimentally extended our previous study of the thermal decomposition of  $\text{CH}_3\text{ONO}$ <sup>5</sup> beyond 550 K, above which the decomposition of  $\text{CH}_3\text{O}$  becomes measurable by either FTIR product analysis in static cell experiments or CW CO laser resonance absorption using a shock tube.<sup>6</sup> Kinetically modeled values of  $k_1$  have also been theoretically interpreted by using the RRKM theory based on the results of our detailed ab initio calculations for reaction 1.<sup>7</sup> These results are briefly reported herein.

### Experimental Section

Two different methods were employed to estimate  $\text{CH}_3\text{O}$  decomposition rates using methyl nitrite as the radical source. In the experiments carried out with a static cell ( $V = 277.3 \text{ cm}^3$ ), various reaction products ( $\text{CH}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ) were quantitatively analyzed by FTIR spectroscopy. A detailed discussion of sampling and the reaction system can be found in ref 5. Typically, 2–4% of  $\text{CH}_3\text{ONO}/\text{He}$  mixtures were pyrolyzed at temperatures between 550 and 700 K within a short time interval and the measured product yields computer-modeled on the basis

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