Combustion and Flame 158 (2011) 618–632

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Roaming radicals in the thermal decomposition of dimethyl ether: Experiment and theory

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ARTICLE INFO

Article history:
Received 19 November 2010
Received in revised form 14 December 2010
Accepted 15 December 2010
Available online 13 January 2011

Keywords:
H+ dimethyl ether
Transition state theory
Ab initio
Shock tube
Abstraction

ABSTRACT

The thermal dissociation of dimethyl ether has been studied with a combination of reflected shock tube experiments and ab initio dynamics simulations coupled with transition state theory based master equation calculations. The experiments use the extraordinary sensitivity provided by H-atom ARAS detection with an unreversed light source to measure both the total decomposition rate and the branching to radical products versus molecular products, with the molecular products arising predominantly through roaming according to the theoretical analysis. The experimental observations also provide a measure of the rate coefficient for $H + CH_3OCH_3$. An evaluation of the available experimental results for $H + CH_3OCH_3$ can be expressed by a three parameter Arrhenius expression as,

$$k = 6.54 \times 10^{-24} T^{4.13} \exp(-896/T)\ \mathrm{cm^3\ molecule^{-1}}\ s^{-1} (273 - 1465\ \mathrm{K})$$

The potential energy surface is explored with high level ab initio electronic structure theory. The dynamics of roaming versus radical formation is studied with a reduced dimensional trajectory approach. The requisite potential energy surface is obtained from an interpolative moving least squares fit to wide-ranging ab initio data for the long-range interactions between methyl and methoxy. The predicted roaming and radical micro-canonical fluxes are incorporated in a master equation treatment of the temperature and pressure dependence of the dissociation process. The tight (i.e., non-roaming) transition states leading to a variety of additional molecular fragments are also included in the master equation analysis, but are predicted to have a negligible contribution to product formation. The final theoretical results reliably reproduce the measured dissociation rate to radical products reported here and are well reproduced over the 500–2000 K temperature range and the 0.01–300 bar pressure range by the following modified Arrhenius parameters for the Troe falloff format:

$$k_{1,\infty}(T) = 2.33 \times 10^{19} T^{-0.661} \exp(-42345/T)\ \mathrm{s^{-1}}$$
$$k_{1,0}(T) = 2.86 \times 10^{35} T^{-11.4} \exp(-46953/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$
$$F_{cent}(T) = \exp(-T/880)$$

The experimentally observed branching ratio of 0.19 ± 0.07 provides a direct measure of the contribution from the roaming radical mechanism. The theoretical analysis predicts a much smaller roaming contribution of 0.02.

1. Introduction

The simplest of the ethers, dimethyl ether (DME), is a synthetic fuel produced commonly from syngas (CO, H_2) and also from a variety of other feedstocks such as coal, natural gas, biomass, and blends of these. When DME burns it is smokeless, and it is therefore a favorable replacement candidate for diesel fuel from an emissions perspective. In addition to being a potential diesel fuel

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doi:10.1016/j.combustflame.2010.12.017

replacement, DME can also be used as (1) a fuel in gas turbines for power generation, (2) an LPG substitute, (3) a hydrogen source for fuel cells, and (4) as a feedstock for chemicals [1]. Recent interest in DME as an alternative fuel and as a potential additive has spurred a number of combustion studies that have been highlighted in a special issue [2].

Thermal decomposition plays a significant role in the combustion kinetics of DME [3]. In all previous experimental studies [4–10] the thermal decomposition of CH_3OCH_3 is presumed to undergo C–O bond fission through R1,

$$CH_3OCH_3 \rightarrow CH_3 + CH_3O \tag{R1}$$

However, recent theoretical studies [11] suggest the ubiquity of roaming radical processes in a variety of molecular systems. For DME, the roaming radical mechanism, if present, will lead to the formation of molecular products, CH_4 and CH_2O, through R2,

$$CH_3OCH_3 \rightarrow CH_3 \cdots OCH_3 \rightarrow OCH_3 \cdots CH_3 \rightarrow CH_4 + CH_2O \tag{R2}$$

The branching between radical (R1) and molecular (R2) products might be expected to have a significant impact on the combustion properties for DME.

Early studies on roaming radical mechanisms considered the photodissociation of small molecular systems. For example, in formaldehyde it was shown that during the process of C–H bond fission some of the departing H-atoms can roam around the HCO moiety at long-range and then abstract a hydrogen atom with no further activation energy to produce H_2 + CO [12]. Subsequent experimental and theoretical studies on acetaldehyde photodissociation demonstrated the presence of an analogous process with a roaming CH_3 radical to give CH_4 + CO [13–15].

The branching to a roaming channel in a thermal dissociation was first identified in a combination of experimental and theoretical studies [16,17] on acetaldehyde. DME represents another potential candidate for an important roaming radical channel in a thermal dissociation. A preliminary scan of the DME potential energy surface reveals that the saddle point for the roaming process ($CH_3 \cdots OCH_3 \rightarrow OCH_3 \cdots CH_3$) is ~2 kcal/mol below the C–O bond fission asymptote. For CH_3CHO, the roaming radical transition state was ~1 kcal/mol below the C–C bond fission asymptote [17]. Consequently, one might expect in DME a similar if not larger contribution from the roaming radical mechanism than in CH_3CHO.

In this work, we employ a combination of experimental measurements and theoretical analyses in a detailed study of the roaming fraction for the thermal decomposition of DME. This analysis is closely related to the prior study of the thermal dissociation of acetaldehyde [16,17]. The experimental component of this work employs the reflected shock-tube technique with a high sensitivity H-atom Atomic Resonance Absorption Spectroscopy (ARAS) detection scheme to minimize secondary reactions and determine absolute yields of products. At high temperatures, CH_3O instantaneously dissociates to H + CH_2O, and, therefore, temporal H-atom measurements are good indicators for the rate of R1.

One aspect of the theoretical analysis involves ab initio transition state theory based master equation calculations of the rate coefficients for the various decomposition processes. This analysis indicates that the channels leading to H_2 + CH_3OCH, H + CH_3OCH_2, and $^1CH_2$ + CH_3OH are kinetically insignificant. As discussed below, the present experimental measurements then directly provide the branching between the C–O bond dissociation channel (R1) and the roaming channel (R2).

The primary focus of the theoretical analysis is on the direct calculation of the roaming fraction as a complement to the experimental measurements of this quantity. These calculations are carried out with a reduced dimensional trajectory (RDT) approach as described in Ref. [17]. The RDT calculations require a six-dimensional potential energy surface describing the interaction between rigid CH_3 and CH_3O radicals for arbitrary orientations and separation. Here, this potential energy surface is generated from a novel application of the interpolative moving least squares (IMLS) fitting approach [18], with the underlying ab initio data obtained from multi-reference second order perturbation theory (CASPT2).

The experimental work adds significantly to the database for DME decomposition. The majority of the prior DME thermal decomposition studies were carried out in flow reactors [4–8]. These studies used large initial concentrations of fuel, and, therefore, the thermal decomposition rate coefficients relied heavily on detailed chemical kinetics modeling. In order to better characterize the high-temperature thermal decomposition rates, two recent studies have been carried out using shock tubes. The Fernandes et al. [9] study used H-atom ARAS as the diagnostic for measuring rate coefficients for R1. By contrast, the Cook et al. [10] study used mixtures of DME in excess O_2 with OH-absorption as the diagnostic. The resulting H-atoms from CH_3O decomposition react with excess O_2 to form OH through the chain branching reaction, H + O_2 → OH + O, and therefore, the OH-temporal profiles can then be used to obtain rate constants for R1.

Both new studies employed analytical techniques that allowed the use of much lower initial concentrations of DME than earlier studies [4–8]; however, they still need to use a chemical kinetic model to extract rate coefficients for R1. Even the H-atom ARAS study of Fernandes et al. [9], with the lowest initial DME concentrations of any published DME kinetics experiment, still used relatively large initial concentrations. As a result, one secondary reaction, namely H + CH_3OCH_3 → products, had a major effect on the long time values of [H]. These authors were able to specify rate constants for this reaction through modeling, and subsequently, also for the thermal decomposition.

Not only are all prior DME kinetics studies complicated by secondary reaction perturbations, but, more importantly for this study, absolute yields for various thermal decomposition channels could not be directly measured. In contrast, the present work uses a higher sensitivity H-atom ARAS detection scheme to minimize secondary reactions, and this allows determinations for absolute yields of products. The resonance light source used in this laboratory is unreversed, giving an increase of ~5–10 in sensitivity over that used by Fernandes et al. [9], who also used the ARAS technique but with a substantially reversed resonance light source [19]. As in earlier work [20], we show that this unreversed source allows experiments to be performed under pseudo-first order conditions; i.e., with no secondary reaction interferences.

We also extend these ultra-dilute pseudo-first order studies to experiments with roughly the same $[CH_3OCH_3]_0$ as Fernandes et al. [9]. These higher concentration experiments expand our rate constant database for DME decomposition to lower-*T*, and allow for the determination of rate constants for H + CH_3OCH_3 via the modeling of the temporal H-atom profiles. The measurements for the H + DME reaction extend the experimental rate database for that reaction to higher-*T* than the recent measurements of Takahashi et al. [21].

2. Experiment

The present experiments were performed with the reflected shock-tube technique using H-atom ARAS detection. The methods and the apparatus currently being used have been previously described [22,23] and only a brief description of the experiment will be presented here.

The shock-tube was constructed entirely from a 7-m (10.2 cm o.d.) 304 stainless steel tube with the cylindrical section being separated from the He driver chamber by a 4 mil unscored