Lawrence Berkeley National Laboratory
Recent Work

Title
Determination of the Barrier Height to CH_{3}CO Dissociation

Permalink
https://escholarship.org/uc/item/9pf3068t

Journal
Chemical Physics Letters, 224(1/2/2008)

Authors
North, Simon W.
Blank, David A.
Lee, Yuan T.

Publication Date
1994-03-22
Submitted to Chemical Physics Letters

Determination of the Barrier Height to CH₃CO Dissociation

S. North, D.A. Blank, and Y.T. Lee

March 1994
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Determination of the Barrier Height to CH$_3$CO Dissociation

S. North, D.A. Blank, and Y.T. Lee

Department of Chemistry
University of California

and

Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

March 1994

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
Determination of the Barrier Height to \( \text{CH}_3\text{CO} \) Dissociation

Simon W. North, David A. Blank, and Yuan T. Lee
Chemical Sciences Division, Lawrence Berkeley Laboratory,
and
Department of Chemistry, University of California, Berkeley, CA 94720, USA

The photodissociation of acetyl chloride at 248 nm has been investigated by the technique of photofragment translational spectroscopy. A comparison of the translational energy distributions required to fit the chlorine atom and the acetyl radical indicates that a significant fraction (~35%) of the \( \text{CH}_3\text{CO} \) fragments undergo secondary decomposition to \( \text{CH}_3 \) and CO. From analysis of the center-of-mass translational energy distributions a value of 17±1 kcal/mole for the barrier height to acetyl radical dissociation has been determined.

I. Introduction

The photodissociation of acetyl chloride at 248 nm has recently been investigated by Person et al. [1,2]. Although the initial transition is a localized \({}^1(n,\pi^*)\) excitation on the CO moiety, the dissociation involves exclusive \(\alpha\)-cleavage of the stronger C-Cl over the C-C bond.

\[
\text{CH}_3\text{COCl} \rightarrow \text{CH}_3\text{CO} (\tilde{X}) + \text{Cl} \left( ^2P_j \right)
\]  \hspace{1cm} (1)

This preference can be understood by a simple consideration of the adiabatic potential energy surfaces for both processes [2]. In this picture the C-Cl bond cleavage occurs adiabatically on a \({}^1A''\) surface which has \(1n\pi^* (C=O)\) character in the Frank-Condon region, and as a result of an avoided crossing the dissociation proceeds over a barrier onto an area which resembles the repulsive np(Cl) \(\sigma^*(C-Cl)\) surface. In contrast, C-C bond fission does not adiabatically correlate to ground state products. It can occur via either a combination of the \(3\sigma^*(C-C)\) and \(3\pi^*(C=O)\) surfaces or on the ground state surface and therefore must be preceded by intersystem crossing or internal conversion.

If the \( \text{CH}_3\text{CO} \) fragment from the primary process contains sufficient internal energy it
can spontaneously dissociate,

$$\text{CH}_3\text{CO} \rightarrow \text{CH}_3 + \text{CO}$$

(2)

The reported barrier to acetyl radical dissociation has ranged from 11.1-21.7 kcal/mole [3]. For small cited values of the barrier height, anomalously low preexponential factors were required to explain the observed rates. These A-factors were rationalized by proposing that acetyl radical decomposed via a non-adiabatic process. Watkins and Word determined the barrier to be 17.2±0.5 kcal/mole from extensive kinetics measurements on the addition of methyl radical to carbon monoxide [4]. They found a preexponential factor, 13.2±0.2 s⁻¹, that was more consistent with this type of reaction. Work in this laboratory on the photodissociation of acetone at 248 nm has yielded a barrier height to acetyl radical dissociation of 17.5±3 kcal/mole [5]. Given this barrier height and the measured translational energy distribution of Person et al. almost 40% of the nascent CH₃CO formed from the dissociation of acetyl chloride should undergo spontaneous secondary decomposition. However, the signal-to-noise ratio in the study by Person et al. was insufficient to observe any secondary decomposition of the CH₃CO photoproducts.

The focus of the present work is to determine the barrier height to CH₃CO decomposition by the method of photofragment translational spectroscopy (PTS). PTS is a technique proven capable of extracting accurate thermodynamic quantities such as bond dissociation energies and barrier heights [6]. Furthermore, by observing the photofragments that originate from spontaneous or photon mediated dissociation of the primary products it is possible to study the dissociation dynamics of transient species under collisionless conditions [7]. The spontaneous decomposition of acetyl radicals in this experiment can be monitored in two ways: 1) since a large portion of the nascent CH₃CO fragments dissociate prior to detection, these missing radicals provide an indication of the energy at which the radicals become thermodynamically unstable, 2) observation of the secondary dissociation products, CH₃ or CO, allows independent confirmation and quantitation of the secondary decomposition of CH₃CO radicals. Using this technique we
have determined the barrier height to dissociation of the acetyl radical.

II. Experimental

The fixed-source/rotatable-detector apparatus used in this experiment is described in detail elsewhere [8]. In brief, 50 torr of 20% acetyl chloride seeded in helium was expanded through a 0.37 mm nozzle into a source region held at 1x10^{-4} torr. The nozzle was heated to 80°C in order to reduce the formation of dimers in the supersonic expansion. The average beam velocity was 10x10^4 cm/s with a FWHM of ~15%. Following expansion the molecular beam was collimated twice and subsequently intersected at a right angle with the unpolarized output of a Lambda Physik EMG101 excimer laser operating at the KrF transition (248 nm). Laser power was maintained between 50-70 mJ/cm^2 and focused with a spherical lens to a 2x5 mm spot in the interaction region. Neutral photofragments recoiled 20.8 cm where they were ionized by electron impact with ~200 eV electrons, mass selected with a quadrupole mass filter, and detected with a Daly ion counter [8]. Time-of-flight (TOF) spectra were collected using a computer interfaced multichannel scaler triggered from the laser with a bin width of 2 \mu s. Center-of-mass translational energy distributions of the photofragments were determined from the TOF spectra using the forward convolution technique [9].

III. Results and Discussion

TOF spectra were collected at m/e=35, 42, and 15 at a variety of detector angles with respect to the molecular beam axis. All observed signals exhibited a linear dependence on the laser power confirming that the observed photodissociation is a single photon process. The TOF spectra for m/e=35 (Cl^+) at detector angles of 15° and 30° are shown in figure 1. The spectra show only a single feature representing the Cl atomic fragment originating from direct C-Cl bond cleavage (eq. 1). There was no evidence of a COCl fragment which, if it were a primary dissociation product resulting from C-C bond cleavage would also be observed at m/e=35 following dissociative ionization. No other signal consistent with primary C-C bond scission was observed, confirming the conclusion of Person et al. that C-Cl bond cleavage is the exclusive primary disso-
Results and Discussion

ciation process. [2] Figure 2 shows the TOF spectra at 15° and 30° for the momentum matched acetyl fragment in equation 1 which was monitored at m/e=42 (CH2CO+), due to enhanced signal to noise as compared with its parent mass.

The translational energy distribution, P(E_T), for the dissociation in equation 1 was determined by forward convolution fitting of the Cl atom (m/e=35) TOF spectrum and is shown as the solid line in figure 3. The distribution is peaked at ~16 kcal/mole and has a FWHM of ~15 kcal/mole which is in good agreement with the P(E_T) reported by Person et al. [2]. In order to fit the CH3CO (m/e=42) TOF spectrum it was necessary to truncate the P(E_T) at 15 kcal/mol as shown by the dotted line in figure 3, leaving only the high energy portion of the translational energy distribution. The fits to the acetyl TOF spectrum with truncation of the P(E_T) occurring at 13.2 kcal/mol and 16.8 kcal/mol are shown in figure 4 demonstrating the sensitivity of the fit to the position of truncation. Truncation of the P(E_T) is the result of primary acetyl photofragments which undergo secondary dissociation (eq. 2). Since the chlorine atom is one of the photoproducts, all energy that is not released into translation must reside as internal energy in the CH3CO fragment. The agreement of the determined barrier height reported here (vide infra) to the one measured in the dissociation of acetone suggests that the dissociation of acetyl chloride at 248 nm leads to Cl formed predominately in its ground spin-orbit state, (2P3/2).

If CH3CO fragments possess internal energies that exceed their barrier to dissociation they will not persist for sufficient time to reach the detector. These radicals with high internal energies, and therefore low translational energies, do not contribute to the parent TOF spectra. In the present case this is manifest as a deviation of the CH3CO P(E_T) from the Cl, or true primary P(E_T). The truncation in the CH3CO P(E_T) represents the maximum internal energy at which the acetyl radical is stable with respect to decomposition. A similar analysis has been used to determine the C-Cl bond dissociation energy in C2H4Cl radicals by Minton et al. [7]. If E_T(min) denotes the value corresponding to the onset of truncation then the barrier to acetyl radical dissociation, E_barr(CH3CO), is given by,
where $E_{hv}$ is the photon energy and $D_0(CH_3CO-Cl)$ is the C-Cl bond energy in acetyl chloride. From the known heats of formation of CH$_3$CO and Cl atoms, a C-Cl bond dissociation energy of 83.0 kcal/mole can be obtained [10]. Given that the $E_{hv}(248\text{nm})$ is 115.0 kcal/mole, the available energy, $E_{avail}$, in the center-of-mass is 32.0 kcal/mole. The best fit to the CH$_3$CO TOF spectra was obtained with $E_T(min)=15$ kcal/mole corresponding to 17±1 kcal/mole for the barrier height to acetyl decomposition. The truncation occurring near the peak in the primary translational energy distribution is significant. Since this region of the $P(E_T)$ constitutes a large fraction of the distribution, the fit to the CH$_3$CO data is very sensitive to the point of truncation. Changing the value of $E_T(min)$ by ±1.8 kcal/mole significantly reduced the quality of the fit to the experimental data (figure 4). This measurement is superior to the analogous one determined from acetone dissociation at 248 nm for two important reasons. First, in acetone dissociation the primary methyl radical, which reflects the true primary $P(E_T)$, is overlapped in the TOF spectrum by contributions from secondary methyl radicals and CH$_3$CO daughter ions. This hinders determination of the primary $P(E_T)$ for the dissociation. Second, the internal energy in the acetone dissociation can be distributed between both the CH$_3$ and CH$_3$CO fragments. Therefore, even at internal energies exceeding the CH$_3$CO barrier to dissociation some of the energy can be accommodated by rovibrations of the CH$_3$ counter fragment. Consequently the truncation in the $P(E_T)$ is less abrupt and makes the assignment of $E_T(min)$ considerably more difficult.

There are several implicit assumptions in eq. 3. Although the average vibrational energy of the parent molecules at 80°C is ~1.4 kcal/mole this should be significantly reduced following the supersonic expansion and has been neglected in calculating the available energy [11]. If the parent vibrations are not fully relaxed then there will be more available energy and would result in a corresponding underestimation of the barrier height. It is also assumed that unstable acetyl radicals, those that possess internal energy in excess of their barrier to dissociation, do not contribute to the CH$_3$CO TOF spectra. This is reasonable since RRKM calculations indicate that acetyl radi-
Results and Discussion

cals with internal energy exceeding their barrier by 0.1 kcal/mole dissociate in $\sim 5 \times 10^{-10}$ s, which is much shorter than the flight time to the detector ($\sim 10^{-4}$ seconds). We have also not considered the effect of rotational metastability of the nascent CH$_3$CO radicals. This was observed to be pronounced in the case of CH$_2$CH$_2$OH originating from the photodissociation of 2-bromoethanol due to the large exit impact parameter [12]. However, based on the measured anisotropy of Butler and coworkers [1,2] and the acetylchloride equilibrium geometry [13], the exit impact parameter is very small. Simple impulsive-type calculations indicate that < 0.2 kcal/mole should appear in CH$_3$CO rotational excitation and the majority of this is coupled to the reaction coordinate.

Further evidence for the secondary dissociation of acetyl fragments is seen in figure 5 which is the TOF spectrum at m/e=15 (CH$_3^+$) with a detector angle of 20°. The TOF spectrum in figure 5 has been fit with two components. The narrow component is from primary acetyl fragments (eq. 1) dissociatively ionizing to form the daughter ion CH$_3^+$. The broad component represents methyl radicals from secondary dissociation of the primary acetyl radicals (eq.2). The methyl fragment component was fit with a secondary P(E$_T$) reflecting the height of the exit barrier ($\sim 6$ kcal/mole) and an angular distribution with forward-backward symmetry. A more detailed description of the secondary process is forthcoming [5]. Comparison of acetyl chloride with acetone at 248 nm suggests that the relative contributions of parent to methyl radical in the m/e=15 TOF spectra is consistent with $\sim 35\%$ secondary dissociation.

This work has demonstrated that a direct measurement of the CH$_3$CO barrier height can be obtained using photofragment translational spectroscopy. Our value of 17±1 kcal/mole is in good agreement with the result of Watkins and Word [4] and is consistent with an independent measurement in this laboratory [5].

Acknowledgments. The Authors would like to thank A. Suits for helpful discussions. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-ACO3-76SF00098 and The Office of Naval Research.
References


11. This is a reasonable assumption. For example at a temperature of 200 K the parent would only contain ~0.3 kcal/mol of vibrational excitation.


Figure Captions

Figure 1: TOF spectra of m/e=35 (Cl⁺) at laboratory angles of (a) 15° and (b) 30°. The open circles represent data and the solid lines are the forward convolution fits to the data using the center-of-mass P(Eₜ) shown in figure 3 (solid line).

Figure 2: TOF spectra of m/e=42 (CH₂CO⁺) at laboratory angles of (a) 15° and (b) 30°. The open circles represent data and the solid lines are the forward convolution fits using the P(Eₜ) in figure 3 truncated at 15 kcal/mol as shown by the dotted line.

Figure 3: Center-of-mass translational energy distributions used to fit the data in figures 1 and 2. Dotted line represents point of truncation used to fit figure 2.

Figure 4: TOF spectrum of m/e=42 (CH₂CO⁺) at a laboratory angle of 30°. The dotted and dashed lines represent the forward convolution fits using the P(Eₜ) in figure 3 truncated at 13.2 kcal/mol and 16.8 kcal/mol respectively (+1.8 kcal/mol as compared to the truncation used to fit the TOF spectra in figure 2).

Figure 5: Time-of-flight spectrum of m/e=15 (CH₃⁺) at 20°. The open circles are the data. The lines are contributions from primary acetyl radicals (- - -) and methyl radicals from secondary dissociation (-----). The solid line is the total fit to the data.
Figure 1

(a) m/e = 35 15 deg.

(b) m/e = 35 30 deg.
Figure 2

(a) m/e=42
15 deg.

(b) m/e=42
30 deg.
Figure 3
Figure 4
Figure 5

Counts

Time (microseconds)

m/e=15
20 deg.