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THE OBSERVATION OF CH₃O IN THE COLLISION FREE
MULTIPHOTON DISSOCIATION OF CH₃NO₂(U) CALIFORNIA UNIV
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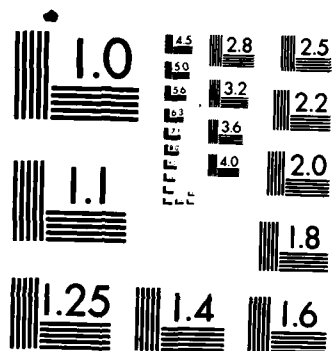
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20. Abstract

The method of infra-red, laser, crossed, molecular-beam, photofragmentation, translational spectroscopy has been used to study the "thermal" chemistry of nitromethane under collision free conditions. We have observed for the first time experimental evidence that shows that the isomerization of nitromethane to methylnitrite is an important thermochemical process in the unimolecular decomposition of the title compound. Based on theoretical predictions of Dewar et.al. that the Arrhenius pre-exponential factor is $10^{13.3}$, we have been able to estimate the potential energy barrier height for the isomerization reaction to be 55.5 ± 1.5 kcal/mol, compared to the C-N bond energy of 59.2 kcal/mol. It is clear that in mechanistic modeling of the thermal decomposition of nitromethane, this important dissociation channel must be taken into consideration. We have also been able to conclusively show that previous suggestions of a dynamical barrier in the exit channel of the simple C-N bond fission reaction are in error.

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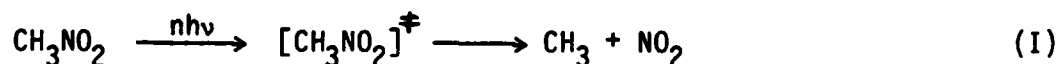
THE OBSERVATION OF CH_3O IN THE COLLISION FREE
MULTIPHOTON DISSOCIATION OF CH_3NO_2

Alec M. Wodtke, Eric J. Hints and Yuan T. Lee

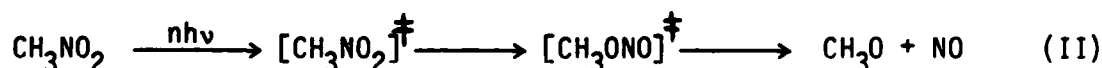
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Although the hope of directing chemical reactions by infra-red multiple photon dissociation (IRMPD) has never been realized, it has provided the impetus for a great deal of work¹⁻¹⁰ in the area of unimolecular decomposition of polyatomic molecules. It has been found in general that IRMPD does not differ greatly from pyrolysis, in many important ways. Some researchers have probed the internal state distributions of the products,²⁻⁵ while others have studied how energy appears in the translational degrees of freedom.⁶⁻¹⁰ In general, for a medium sized polyatomic molecule, the lowest energy dissociation pathway is found to be the most important one and the dissociation process can be adequately described by statistical theory.¹¹ In particular, statistical theory predicts that for simple bond rupture reactions where no exit barrier exists, the probability distribution for translational energy release, or $P(E_T)$, should be a monotonically decreasing function of translational energy peaking toward zero and overall releasing only a small fraction of the available energy as translation.^{7,8} In the case of molecular elimination channels, very often the presence of substantial exit barriers due to repulsion between the closed-shell products causes a larger amount of energy to go into translation and the $P(E_T)$ may peak away from zero. The observation of such translational energy distributions has been taken as

evidence of exit barriers in the potential energy surface.^{9,10} Since reaction I, the simple bond rupture of nitromethane is not expected to have



an exit barrier, it came as a surprise that the $P(E_T)$, measured by the multiphoton-ionization time-of-flight (MPI-TOF) method, appeared to peak at ~8 kcal/mole.¹² In view of the anomalous results of this translational energy measurement and in order to test the validity of the recent theoretical suggestion¹³ that reaction II, isomerization to methyl nitrite and subsequent decomposition to CH_3O and NO , should be competitive with



reaction I, we undertook to study the IRMPD of nitromethane with a newly constructed molecular beam machine, specifically designed for photofragmentation translational spectroscopy.¹⁴

The experimental arrangement is similar to the one described recently.¹⁴ Briefly, a continuous, seeded, molecular beam of nitromethane was produced by passing 145 torr of He through a 24°C bath of nitromethane (Mallinkrodt spectral grade) and delivering the mixture to a 580°K heated nozzle with a diameter of 125 μm . The heating eliminates cluster formation and enhances multiple-photon absorption. This gave a peak beam velocity of 1.3×10^5 cm/sec. The nitromethane was dissociated by a 100 J/cm² pulse of IR light originating from a GENTEC TEA-CO₂ laser operating on the R(20) line of the 9.6 μm branch. This gave a photon energy of 1078 cm⁻¹. The TOF spectrum over a 38 cm flight path was recorded by sampling the mass-filtered ion signal on a 255 channel scaler. The laser operated at 35 Hz

and typically 500,000 laser shots produced a TOF spectrum of adequate signal-to-noise. Signal was observed at masses 46, 30, 29, and 15.

Fig. 1a shows the resulting TOF spectrum for mass 46 (NO_2^+), originating from NO_2 fragments, at an angle of 10° from the molecular beam. The $P(E_T)$ shown in fig. 2 (lower scale) generates the solid curve in fig. 1a which fits the data. It is clear that the data give no indication of an 8 kcal/mole release of translational energy. This supports the conclusion that there is no exit barrier for reaction I and is in contrast to the results of reference 12, which predict the dashed curve for the NO_2^+ TOF spectrum shown in fig 1a.

If reaction I is the only important dissociation channel, we expect that the mass 30 (NO^+) TOF data should look the same as that of mass 46 since both ions are electron-impact fragments of the same neutral molecule, NO_2 . However, the TOF spectrum of mass 30, shown in fig. 1b clearly indicates that in addition to the contribution from NO_2 shown by the dashed-dot curve, there is a contribution due to a second reaction channel producing NO with significantly higher velocity and shown by the dashed curve. The existence of a second reaction channel is further confirmed by the observation of products detected at mass 29 (HCO^+), shown in fig. 1c. The observation of NO and a product which yields HCO^+ is evidence for the competitive existence of reaction II as suggested in ref. 13.

We attempted to but did not observe the parent ion for CH_3O at mass 31. However, it is not expected that electron impact ionization of CH_3O should yield mass 31. This is because of the high exothermicity for molecular hydrogen elimination from the methoxy cation CH_3O^+ to give H_2 and HCO^+ .¹⁵ The fast part of the mass 30 TOF shown as the

dashed curve in fig. 1b and the entire mass 29 TOF are momentum matched by the mass ratio of the products in reaction II and can be fit by the $P(E_T)$ shown by the upper scale of Fig. 2. Reactions I and II were found to be the only important dissociation channels in CH_3NO_2 . Careful analysis of the experimental results, taking into consideration the relative: ionization efficiencies, electron-impact fragmentation ratios and the conversion from the laboratory to the center-of-mass frame of reference, gives a branching ratio for reaction II:I of 0.6 ± 0.2 . Previously, the formation of CH_3O in the decomposition of nitromethane had been assumed to proceed through secondary reactions of CH_3 with NO_2 . This work is the first experimental evidence for the importance of reaction II under collision free conditions.

Recently, the observation of reactions analagous to II for nitrobenzene and nitrotoluene has been concluded from flow studies.¹⁶ Reactions such as II are actually thermodynamically lower in energy than simple bond fission and should only be unimportant when the barrier to isomerization is significantly higher than the C-N bond energy. The Arrhenius A factor for the isomerization reaction is calculated to be $10^{13.3}$.¹³ Based on this result and RRKM calculations the barrier height to isomerization which matches the observed branching ratio is 54 ± 2 kcal/mol. This is to be compared with a C-N bond dissociation energy of 59.4 kcal/mol in nitromethane.

ACKNOWLEDGMENT

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107 kcal/mol O-H bond energy in H_2COH^+ and assuming the C-H bond in H_3CO^+ is 27 kcal/mol, the same as in H_2CO^+ . This gives an exothermicity of 47 kcal/mol for molecular hydrogen elimination from H_3CO^+ .

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FIGURE CAPTIONS

Fig. 1: TOF spectra. a) Mass 46 (NO_2^+): The circles are the data points. The solid curve is the fit to the data using the $P(E_T)$ from the lower scale of fig. 2. The dashed curve is the prediction based on the results of Ref. 12. b) Mass 30 (NO^+): The dashed-dot curve is the contribution from reaction I and is calculated from the $P(E_T)$ in the lower scale of fig. 2. The dashed curve is the contribution from reaction II and is calculated from the $P(E_T)$ from the upper scale of fig. 2. c) Mass 29 (HCO^+): Ion fragment of CH_3O radical, solid curve is fit to the data based on $P(E_T)$ from upper scale of fig. 2.

Fig. 2: Translational Energy Distributions. Lower scale: distribution for reaction I. Upper scale: distribution for reaction II. Units are in kcal/mol.

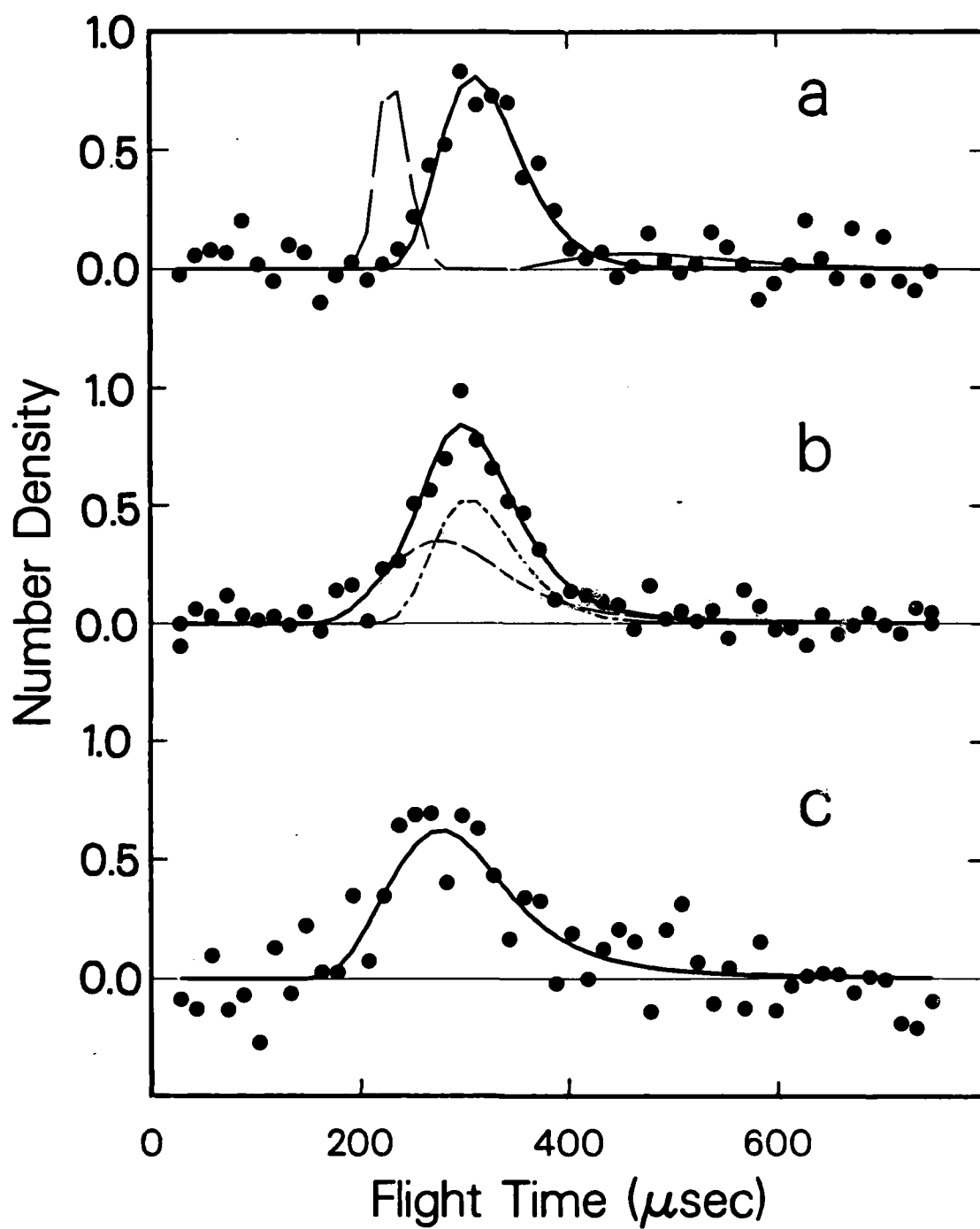
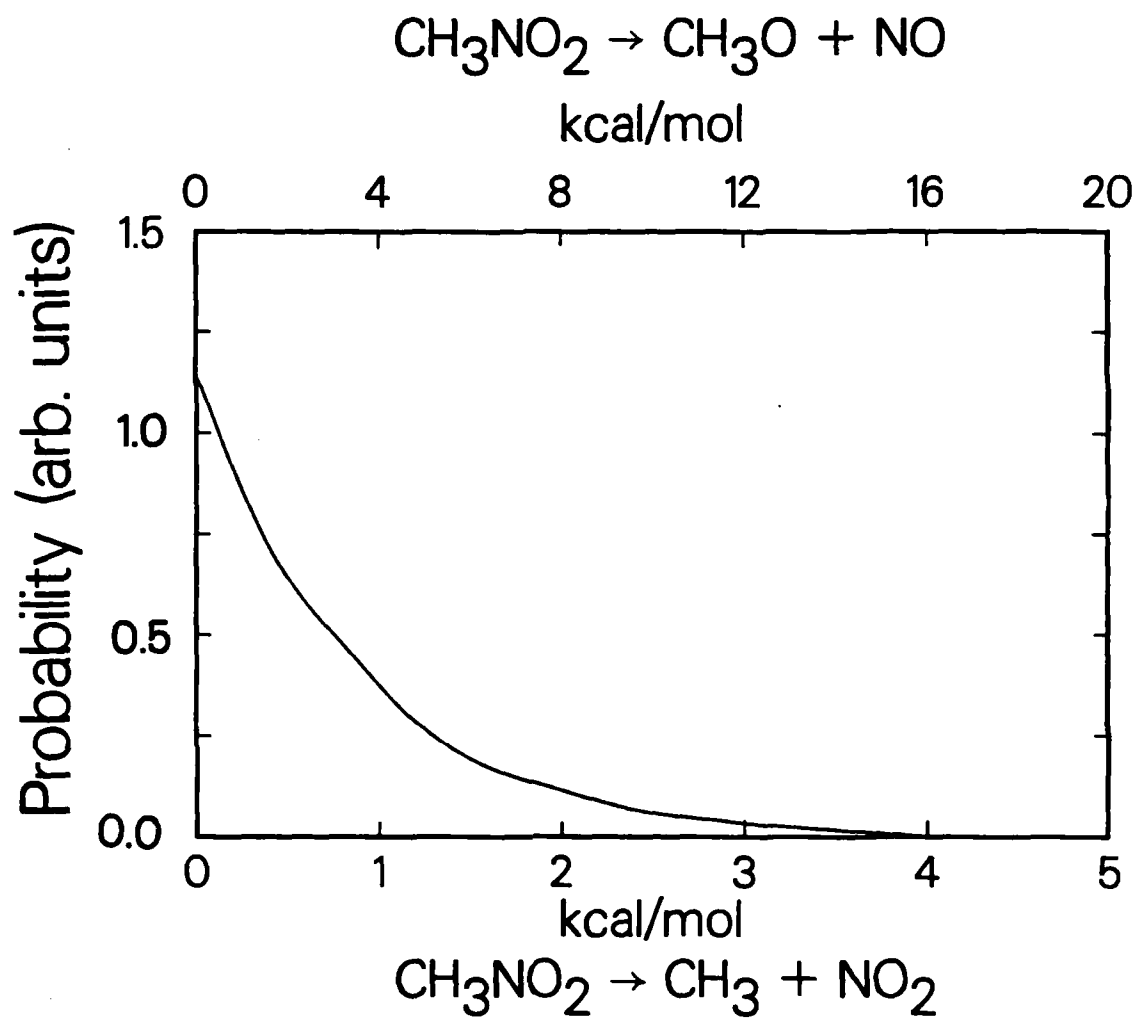


Fig. 1

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Fig. 2

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