AD-A265 588 REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

(2)

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 5/27/93	3. REPORT TYPE AND DATES COVERED Technical Report

4. TITLE AND SUBTITLE

Vibrational overtone activation of methylcyclopropene

5. FUNDING NUMBERS

N00014-88-K-4130
4131063

6. AUTHOR(S)

Geoff Snavely, Salah Hassoon and D.L. Snavely

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Bowling Green State University
Bowling Green, OH 43403

8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report No. 12

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

93-12861

10P8

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

This document has been approved for public release and sale: its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The photoisomerization of 1-methylcyclopropene (MCPene) was studied at specific internal energies accessed by laser vibrational overtone activation. The vibrational overtone spectrum of the 6-0 and 5-0 CH stretches were observed for our synthesized mixture of 75% MCPene and 25% methylenecyclopropane (MCPane). The overtone spectrum of neat MCPane was determined in the spectral regions. The transition wavenumbers were compared to the previously known members of the vinyl, methylenic and methyl vibrational progressions. Product yields from activation through the 5-0 vinyl and methyl CH stretches were determined using gas chromotography. Product ratios of 1,3-butadiene to 2-butyne were measured as a function of pressure and compared to the RRKM predicted yields. After careful measurements we conclude that at these photolysis energies methylcyclopropene does not produce methylene cyclopropane.

14. SUBJECT TERMS

93 6 08 049

Overtones, Methylcyclopropene, Kinetics

15. NUMBER OF PAGES

8

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT N00014-88-K-4130

R&T Code 4131063

Technical Report No. 12

Vibrational overtone activation of methylcyclopropene

by

Geoff Snavely, Salah Hassoon and Deanne Snavely

Prepared for Publication

in

Journal of Physical Chemistry

Center for Photochemical Sciences
Bowling Green State University, Bowling Green, Ohio 43403

May 27, 1993

Vibrational Overtone Activation of Methylcyclopropene

Geoff Snavely, Salah Hassoon and Deanne L. Snavely
Department of Chemistry
Bowling Green State University
Bowling Green, Ohio 43403

Abstract

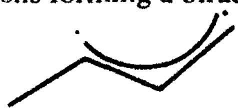
The photoisomerization of 1-methylcyclopropene (MCPene) was studied at specific internal energies accessed by laser vibrational overtone activation. The vibrational overtone spectrum of the 6-0 and 5-0 CH stretches were observed for our synthesized mixture of 75% MCPene and 25% methylenecyclopropane (MCPane). The overtone spectrum of neat MCPane was determined in the spectral regions. The transition wavenumbers were compared to the previously known members of the vinyl, methylenic and methyl vibrational progressions. Product yields from activation through the 5-0 vinyl and methyl CH stretches were determined using gas chromotography. Product ratios of 1,3-butadiene to 2-butyne were measured as a function of pressure and compared to the RRKM predicted yields. After careful measurements we conclude that at these photolysis energies methylcyclopropene does not produce methylene cyclopropane.

Introduction

Vibrational overtone activation of chemical reactions[1] produces activated molecules with well defined internal energies[2] suitable for gaseous unimolecular reaction studies. Vibrational energies near the activation barriers can easily be selected with this technique. The effects of energy transfer are more easily observed at the barrier[3] than at higher excitation energies. the barrier acts as a chemical switch since molecules whose energy falls below the barrier through collisional energy transfer no longer react. For example, in the isomerization reaction of methyl isocyanide[3] the Stern-Volmer plots curve at low pressure. The direction of this curvature reverses depending on which vibrational overtone is used for the photoactivation. The curvature is a result of the competition at the reaction barrier between the collisional energy transfer and the isomerization reaction. This curvature was observed in the 1 to 30 torr pressure range for the methyl isocyanide reaction because the reaction barrier is low (about 37 kcal/mole) and the rate coefficient is high (around 10^8 sec^{-1}). The curvature is a "barrier phenomenon" which will decrease as the photolysis energy increases.

Collisional energy transfer parameters can be measured with vibrational overtone activation[3,4,5]. The slope of the Stern-Volmer plot changes with collider gas reflecting the changed energy transfer environment. Ratioes of the slopes yield the collisional energy transfer efficiency[5] and the average amount of energy transfered per collision, ΔE, can be determined from master equation simulations of the data.

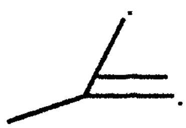
The ring opening reaction of methylcyclopropene (MCPene, **1**) produces three products: 2-butyne (**2**), 1,3-butadiene (**3**) and 1,2-butadiene (**4**) [6]. At total pressures of 20 torr, the kinetics of this ring opening reaction was investigated[7] using MCPene diluted in n-butane to avoid dimerization or polymerization. It is believed to involve a common intermediate for all three reaction products. In this scheme the cyclopropene ring opens forming a biradical (**5**)



5

which then undergoes one of three possible hydrogen shift reactions to form product. Formation of these products via homogeneous unimolecular reactions has been documented[7] with the following activation barriers: 37.8± 0.37 kJ/mol, 2-butyne; 42.2±0.7 kJ/mol, 1,3-butadiene; 43.8±1.5 kJ/mol, 1,2-butadiene. The stabilites of these three products have reversed order with 1,3-butadiene being the most stable (-32.3 kcal/mol), 1,2-butadiene being the least stable (-19.4 kcal/mol) and 2-butyne lying intermediate (23.5 kcal/mol).

Another possible biradical intermediate (**6**) has been suggested which leads to a carbene



6

and subsequent insertion to yield methylenecyclopropane (**7**). MCPane has not been observed as a product in this reaction; however, it is believed that the carbene intermediate does form during thermolysis.

Since **5** and **6** are implicated in this reaction profile perhaps vibrational overtone activation can be used to create a vibrationally excited species which resembles one or the orther of these two intermediates. Using selective excitation of a particular CH stretch within the molecule, we may be able to influence the product yield ratios. This report documents the first results in our complete investigation of the effect of excitation wavenumber and collision partner of the product yirld ratios for this system of three competitve unimolecular reactions.

The ring opening of MCPene has been studied using vibrational overtone activation [8,9] using the 6-0 vinylic CH excitation. Baggott and Law found the measured product yield ratio of 1,3-butadiene to 2-butyne, y_3/y_2, in the total pressure range of 1 to 5 torr was independent of pressure but smaller than that calculated by RRKM theory. The difference in the experimental and calculated product ratio was attributed to inefficient collisional energy transfer. Unfortunately the value of the calculated ratio was not strongly dependent on the magnitude of ΔE and could not be used to determine the collisional energy transfer parameters. However, the ΔE values were determined from a master equation fitting of the experimental quantum yield versus pressure. The overall conclusion of this work was that the results at the vinyl excitation behaved according to RRKM theory.

Samarasinghe and Snavely[9] measured the dissappearence rate of MCPene with photolysis into the 6-0 vinyl CH stretch and calculated the specific rate coefficient for the reaction from the Stern-Volmer plot.

Experimental

1-Methylcyclopropene was prepared according to the procedure developed by Fisher and Applequist[10]. Following the synthesis the product was purified using several bulb-to-bulb vacuum distillations. at liquid nitrogen temperature. Further distillation was required to enhance the purity of the methylcyclopropene/methylenecyclopropane mixture using water/ice temperature and collecting the sample at dry ice/isopropanol temperature. The distillate was collected over a 24-48 hour period in these high temperature distillations. This procedure was repeated a second time before storing the product under vacuum at liquid nitrogen temperature.

The identification and relative purity of MCPene including the major contaminant, MCPane, was analyzed by nmr and gas chromatography (GC). Although the absolute purity of the synthesis product was unknown, a close approximation could be assumed upon the comparison of peak areas from the GC analysis for reactants and solvents from the synthesis. The final purified mixture was about 65% MCPene, 25% MCPane, and 10% tetrahydrofuran, 3-chloro-2-methylpropene, 2-butyne, 1,3-butadiene, and others of decreasing amounts in that order.

Product analyses were conducted on a Hewlett Packard Gas Chromatograph outfitted with a stainless steel, 30 ' X 1/8 " OD, β,β'-oxydipropiononitrile-bonded porasil column and flame ionization detector. Samples were collected prior to injection onto an evacuated gas sampling loop cooled to liquid nitrogen temperature. Peak areas were quantified using a Hewlett Packard Integrator interfaced to the GC.

For the thermolysis study the starting compounds were collected in a glass sample cell insulated so that temperatures ranging from 100 to 230°C could be achieved. Thermolyses were repeated for various pressures and analyzed by GC.

The photoisomerizations were performed in a glass sample cell with quartz windows set at Brewster's angle. The cell was placed intracavity of a dye laser pumped by an argon laser, and the contents photolyzed for a pre-determined amount of time at constant power. At low pressures (between .1 and 2 Torr) photolysis duration was one hour, while at higher pressures, photolyses lasted two or three hours depending on the power output of the dye laser at the photolysis frequency. This procedure was repeated for pressures ranging from 0.1 to 8 torr. The fourth and fifth vibrational overtones corresponding to the methyl, methylenic and vinyl CH local modes were used in the photoylses. Rhodamine 6G and pyridine 2 dyes were used for these photolyses.

Results

a. Spectroscopy

MCPene posseses three methyl, two methylenic and one vinyl CH stretches which should appear at characteristic wavenumbers in the visible vibrational overtone spectrum. We have added to the previously reported data[8,9] finding complete consistency with both data sets. The new absorption wavenumbers and assignments are tabulated in Table 1 along with the new mechanical frequencies and anharmonicities. The spectrum of neat MCPane was recorded confirming the assignments made previously.

b. Kinetics

The product yield ratios for 1,3-butadiene to 2-butyne, y_3/y_2, are plotted versus total pressure for the 6-0 methyl (in plane) and olefinic CH stretch photolyses in Figure 1 and 2. The ratios are independent of pressure up to about 5 torr and then curve downward indicating a higher yield of 2-butyne at higher pressures. The average low pressure experimental y_3/y_2 for the 6-0 olefinic CH was 0.336 which compares very well to that reported by Baggott and Law. Our average experimental y_3/y_2 for the methyl (in plane) CH stretch photolysis was 0.224. This means that at a lower photolysis energy, less 1,3-butadiene was produced relative to the 2-butyne. This is as expected since the barrier to 1,3-butadiene is higher.

c. Thermolysis of MCPene and MCPane

Previously it was reported that methylcyclopropene undergoes a surface induced isomerization to methylenecyclopropane[8]. If this was the case our kinetic model would have to reflect this additional loss of MCPene. We checked for thermolysis of MCPene to MCPane in two ways: monitoring by GC the purity of the starting material over time and allowing the starting material to sit in the photolysis cell for 6 hours. No increase in the MCPane was observed.

In addition we investigated the possibility of thermolysis of MCPane at low energy, taking care to observe MCPene should it occur. These thermolyses were carried out at a total pressure of 1 to 5 torr in a closed pyrex tube outfitted with a Teflon stopock. The cell was held at 230 C for 1/2 to 2 hours followed by the standard GC analysisanalyze the product yield. No products were observed.

Discussion

For vibrational overtone activation the reaction scheme is usually simplified by assuming a single strong collision model. If this is the case then the Stern-Volmer plots are straight lines with slopes proportional to the collisional deactivation rate constant divided by the specific rate coefficient. In the case where several products are produced from a common intermediate the product ratios are given by the ratios of the specific rate coefficients for the particular products. In the case of MCPene the ratio y_3/y_2 should be 0.36 for the photolysis at 17093 cm^{-1} and 0.25 for the photolysis at 15893 cm^{-1}. These values were estimated from the specific rate coefficient curves from Reference 8. Our experimental ratios are independent of pressure and are lower than the calculated ratios.

Baggott believed that if the product ratios were independent of pressure then the reaction was behaving according to RRKM theory. However his plot from the master equation calculated using RRKM rate constants does curve at low pressures. This y_3/y_2 versus collision frequency plot curves at low pressures indicating an increased yield of 1,3-butadiene. We believe that at low pressure these product ratio plots should curve. The overall yield of the product with the higher activation barrier should increase at low pressure since at high pressure the collisional deactivation would most likely deactivate it first. All product ratio plots will curve at low pressure reflecting the increased yield of the product with the higher barrier. For the case of MCPene the curvature is below 1 torr and could not be seen in our experimental results.

Conclusions

The product ratios of 1,3-butadiene to 2-butyne for the ring opening reaction of methylcyclopropene have been measured using vibrational overtone activation to activate the olefinic and methyl (in plane) CH stretches. The product ratios are independent of pressure in the range from 1 to 8 torr. The experimental ratios are lower than those predicted by RRKM theory for these two excitations. The difference between the experiemtnal and calculated values is due to collisional deactivation which decreases the yield of 1,3-butadiene. Work is in progress to measure these ratios for other excitations in methylcyclopropene and other collision partners.

References

1. K.V. Reddy and M.J. Berry, Chem. Phys. Letters 52, 111 (1977).
2. F.F. Crim Ann. Rev. Phys. Chem. 35, 657 (1984).
3. S. Hassoon, N. Rajapakse and D.L. Snavely, *J. Phys. Chem.*, **96**, 2576 (1991).
4. J.E. Baggott, Chem. Phys. Letters 119(1), 47 (1985); J.E. Baggott and D.W. Law, J. Chem. Phys. 85(11), 6475 (1986).
5. D.L. Snavely, R.N. Zare, J.A. Miller and D.W. Chandler, *J. Phys. Chem.* **90**, 3544 (1986).
6. R. Srinivasan, J. Amer. Chem. Soc. 91(23), 6250 (1969).
7. H.Hopf, G. Wachholz and R. Walsh, *Chem. Ber.* 118, 3570 (1985).
8. J. E. Baggott and D.W. Law, J. Chem. Phys. 88(2), 900 (1988).
9. S. Samarasinghe and D.L. Snavely, Chem. Phys. Letters, 150(5), 386 (1988).
10. F. Fisher and D.E. Applequist, J. Org. Chem. 30, 2089 (1965).

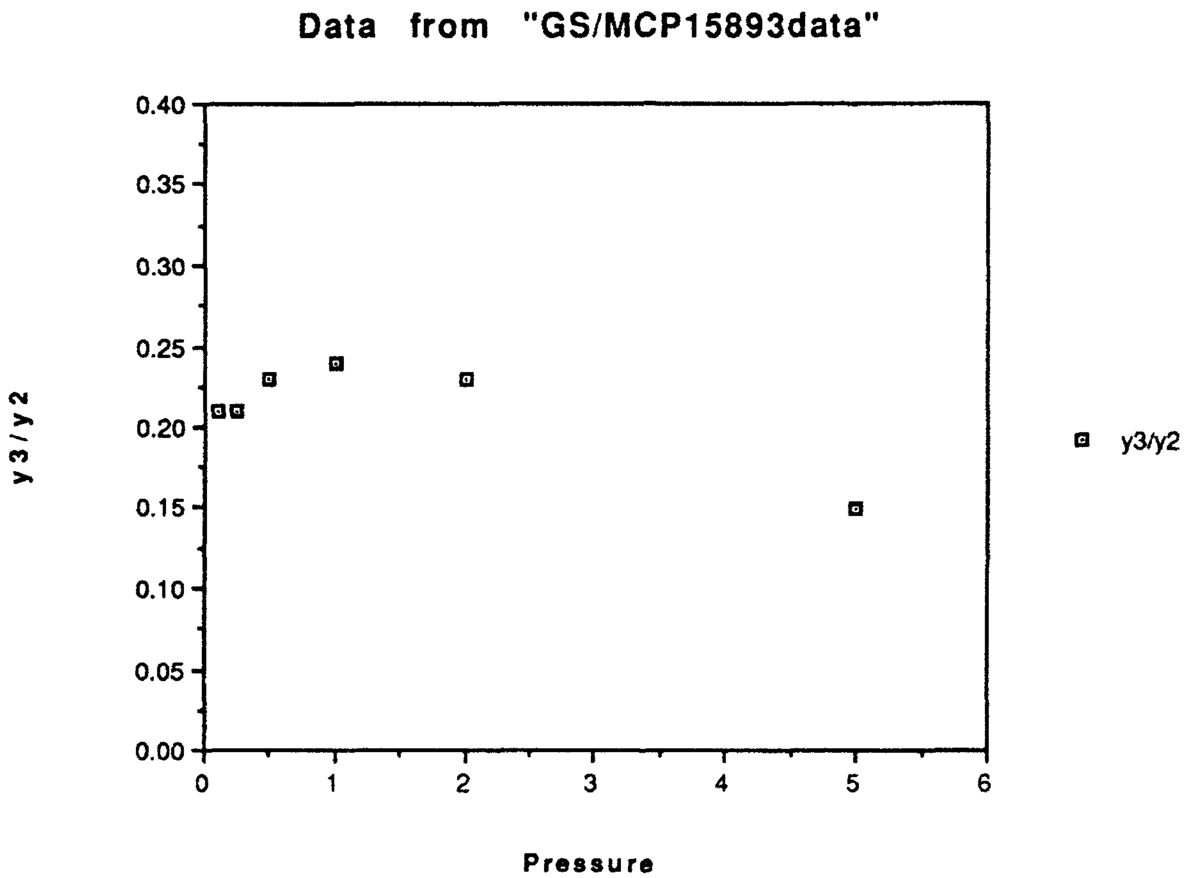
Table 1 Vibrational Wavenumbers of Methylenecycloporpane

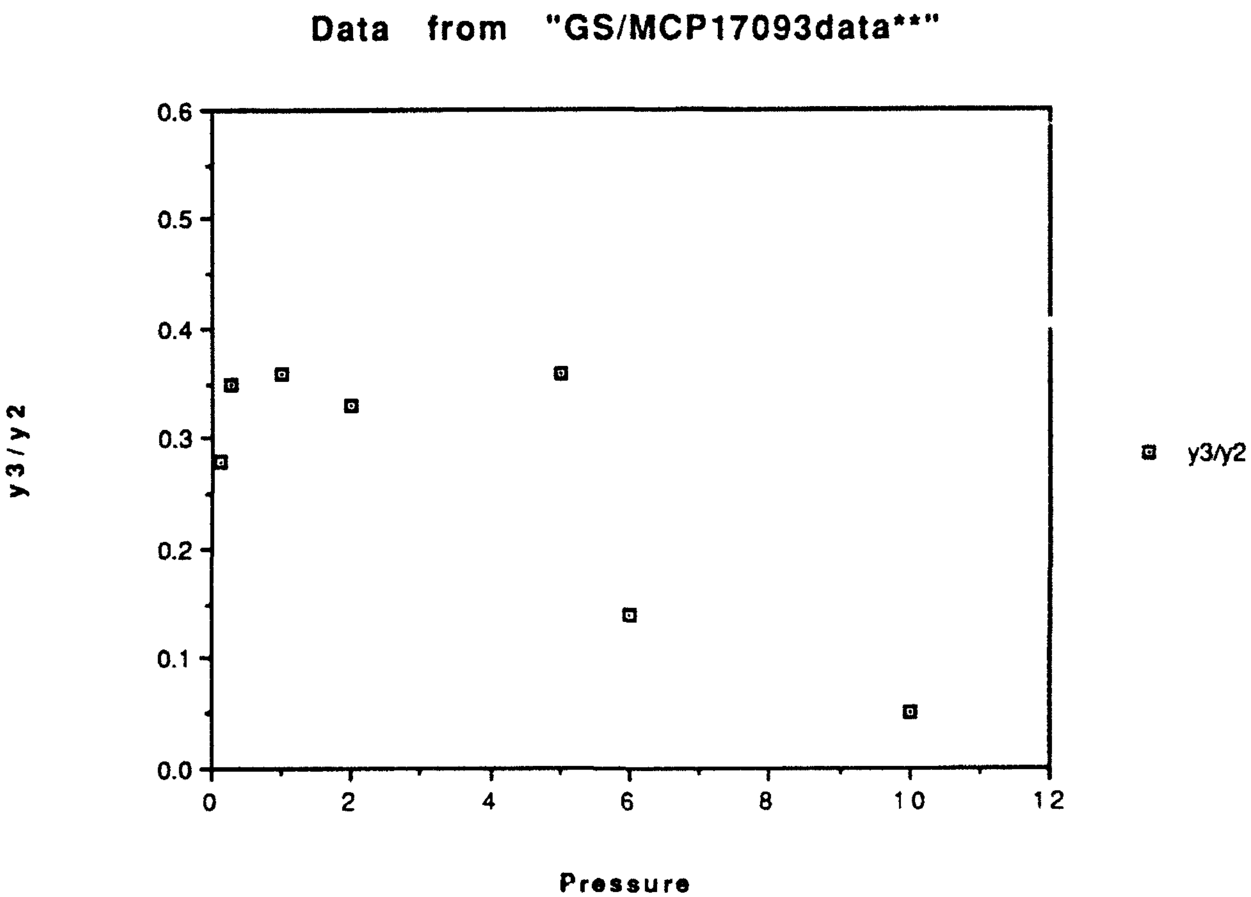
11497 cm^{-1}
11595
11800
11875

Figure Captions

Figure 1 Product yield ratios for photolysis on the methyl CH

Figure 2 Product yield ratios for photolysis on the olefinic CH


Data from "GS/MCP15893data"
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6
y3/y2
Pressure
y3/y2


Data from "GS/MCP17093data**"
0.6
0.5
0.4
0.3
0.2
0.1
0.0
y 3 / y 2
0
2
4
6
8
10
12
Pressure
y3/y2