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Abstract

Laser vibrational overtone activation has been used to investigate the reaction channel competition in the isomerization of 1-methylcyclopropene (MCPene). The vibrational overtone activation of three types of CH stretches (methyl, methlenic and olefinic) in the $6\nu_{CH}$ transition was initiated and all three products (2-butyne, 1,3-butadiene and 1,2-butadiene) were detected by gas chromatography. Stern-Volmer plots have been constructed for the appearence of each individual product and the derived experimental specific rate coefficients compared to those of RRKM theory. Product ratios of 1,3-butadiene to 2-butyne were independent of pressure. These ratios were compared to the RRKM ratios. The product yield ratio for the methylenic photolysis compared well with the RRKM ratio but the olefinic product yield ratio was approximately 40% lower than the RRKM ratio. The implications of these comparisons are discussed.

Introduction

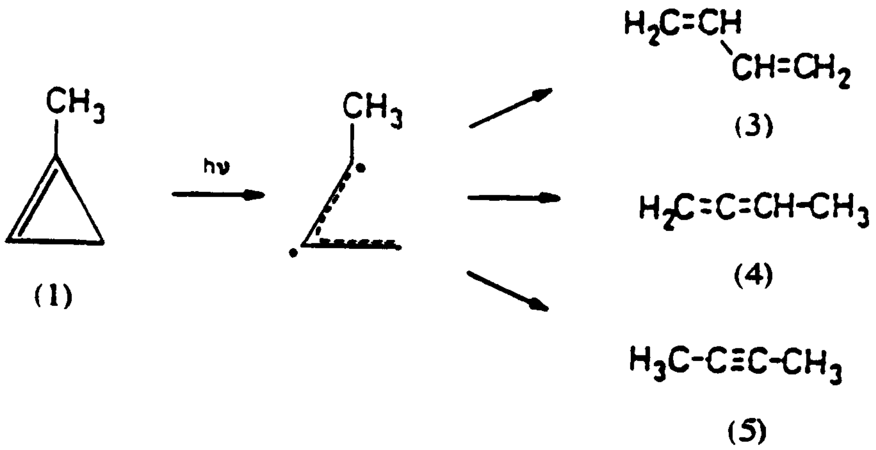
Thermal isomerizations of MCPene have been conducted and studied by Srinivasan[1] and by Hopf, Wachholz and Walsh[2]. The major products reported, in order of diminishing amounts, were: 2-butyne; 1,3-butadiene; and 1,2-butadiene. From Hopf's work, energies of activation (E_a's) for each of the three products are given (units= kcal mol^{-1}): 37.8 for 2-butyne, 42.2 for 1,3-butadiene, and 43.8 for 1,2-butadiene.

Srinivasan[1] reported that in condensed phases of MCPene, a polymerization reaction occurs, and it may also occur to a slight extent in the gas phase. Although Srinivasan did not detect the presence of methylcyclopropane, MCPane, following synthesis of MCPene, Baggott and Law[3] have reported that approximately 38% of the synthesis product was MCPane. Hopf *et al.* [2] reported that 15% of the synthesized product was MCPane. Nearly identical vapor pressures, boiling points and chromatographic behaviors make these two compounds quite difficult to separate.

The ring opening of MCPene has been studied using vibrational overtone activation [3,4] 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[4] measured the disappearance 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. Their result was 1.66×10^{8} sec^{-1} for the reaction.

The unimolecular reaction methylcyclopropene to produce 2-butyne, 1,3-butadiene and 1,2-butadiene (Figure 1)

Figure 1. Proposed mechanism for the isomerization of 1-methylcyclopropene.



proceeds through three competitive reaction channels from the activated complex according to the following equations:

MCP ------> MCP* K_a

MCP* ------> 2-butyne K_2

MCP* ------> 1,3-butadiene K_{13}

MCP* ------> 1,2-butadiene K_{12}

MCP* + M ------> MCP K_d

where K_a is an photoactivation constant, K_d is a collisional deactivation constant at a collision frequency at 1 torr. The product formation is described by first-order kinetic equations which are independent of the other channels.

$$d[P_i]/dt = K(E)_i\,[A^*] \qquad (1)$$

$$Y_i = (d[A_i]/dt)/I \qquad (2)$$

where P_i is the i-th product concentration, I is the number of absorbed photons and Y_i is the yield of an i-th product. The derivative in (1) is constant because the concentration of A* is constant in terms of the steady-state approximation treatment.

From the above considerations the reaction kinetics can be described using the general form of the Stern-Volmer equation where K_{app} shows the rate of appearance of all three products:

$$1/K_{app} = 1/K_a + K_dM/K_a[K(E)_2 + K_2(E)_{13} + K(E)_{12}] \qquad (3)$$

where M is overall pressure in the reaction vessel. One can see from (1) and (2) that the ratio of K(E)'s is proportional to the ratio of the product yields and, hence, to the ratio of the integrated gas chromatography peaks for the product measurements. Since

$$K_i(\varepsilon)/K_j(\varepsilon) = Y_i/Y_j = A_i/A_j \qquad (4)$$

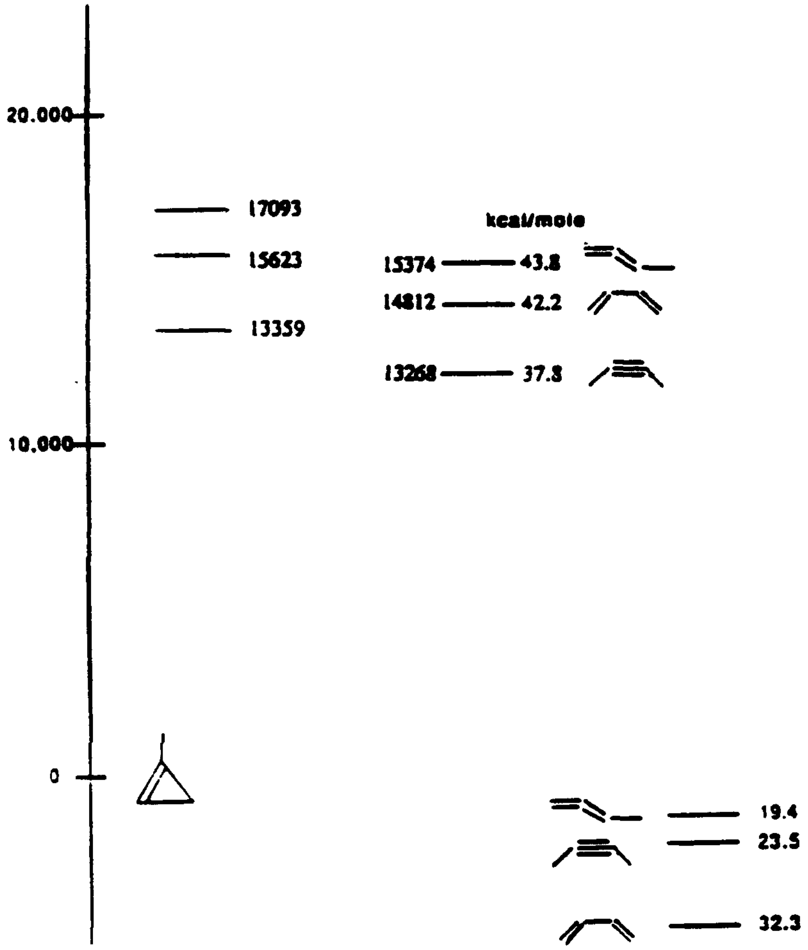
using (1) and (2) the following equation can be derived:

$$1/K_{app} = 1/K_a + K_dM/K_aK_i(\varepsilon)(\Sigma A/A_i) \qquad (5)$$

This equation describes an i-th channel of the unimolecular reaction. Then plotting $1/K_{app}$ versus $MA_i/\Sigma A_i$ yields the specific rate coefficient for an i-th channel. $MA_i/\Sigma A_i$ can be interpreted as the partial pressure of an i-th product in the mixture.

The overtone spectra of MCPene/MCPane in the 5-0 and 6-0 transition regions have been previously recorded and assigned by Samarasinghe and Snavely[4]. The large peaks at 13359 cm^{-1} in the 5-0 transition and at 15623 cm^{-1} in the 6-0 transition were assigned as the methylenic C-H stretch. The two smaller, overlapping peaks to the blue of the methylenic, at 13436 and 13582 cm^{-1} (5-0), and at 15736 and 15893 cm^{-1} (6-0), were assigned as the methyl out-of-plane and the methyl in-plane stretches, respectively. The single peak to the far blue of the 6-0 transition, at 17093 cm^{-1}, was assigned as the olefinic (vinyl) stretch. Figure 2 displays the energy diagram for the overtone activation of 1-methylcyclopropene.

Figure 2 Energy diagram for the overtone activation of 1-methylcyclopropene. (left side) energy scale and three photolysis wavelengths in cm^{-1}. (upper right) activation energies in kcal mol^{-1} and corresponding energies in cm^{-1}. (lower right) relative stabilities of the products in kcal mol^{-1}. (lower left) relative zero of energy for the reactant.



Experimental

1-Methylcyclopropene was prepared according to the procedure developed by Fisher and Applequist[5]. 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 95% MCPene, 5% MCPane, and small impurities of tetrahydrofuran, 3-chloro-2-methylpropene, 2-butyne and 1,3-butadiene 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 0.1 and 2 Torr) photolysis duration was one hour, while at higher pressures, photolyses lasted two or five 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 6 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 DCM dyes were used for these photolyses.

Results and Discussion

Figures 3 through 5 display the Stern-Volmer plots for the 15623, 15898 and 17093 cm^{-1} photolysis, respectively, for the production of 2-butyne, 1,3-butadiene and 1,2-butadiene. The experimental k(E) values calculated from the Stern-Volmer slopes using a hard sphere collisional deactivation constant of 8.28 X 10^6 Torr/s, are tabulated in Table 1. The theoretical logK(E) are also tabulated. The comparison of experimental to theoretical specific rate constants is good for all three products.

Table 1 Experimental Specific Rate Coefficients conpared to RRKM Specific Rate Coefficients

	Experimental specific rate coefficient logK(E), (K(E), RRKM)		
Wavenumber, cm^{-1}	2-butyne	1,3-butadiene	1,2-butadiene
15623	6.201 (6.070)	5.135 (5.100)	4.680 (4.750)
15895	6.425 (6.200)	5.600 (5.480)	5.177 (4.750)
17093	6.691 (6.730)	6.014 (6.250)	5.679 (5.783)

Figure 6 compares our data for the overall disappearence of MCPene to that of Baggott. This comparison indicates that we observed a larger Stern-Volmer slope than that of Baggott resulting from lower product yields. A possible explanation is that our MCPene reactant was more pure being 95% compared to Baggott's 61%. Since the self collider is more efficient our sample would be expected to have a larger slope.

The product yield ratios for 1,3-butadiene to 2-butyne, y_3/y_2, are plotted versus total pressure in Figure 7. The ratios are independent of pressure. The average values for the experimental y_{13}/y_2 are 0.213 and 0.101 for the 17093 and 15623 cm^{-1} photolysis, respectively. 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. 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.The zero pressure product ratios can be determined by the ratio of the RRKM rate coefficients at these photolysis energies. Figure 8 represents this ratio over the entire energy range. The values at 17093 and 15623 cm^{-1} are 0.38 and 0.11, respectively. The lower energy methylenic photolysis agrees with the RRKM ratio. For the higher energy photolysis the product yield ratio does not agree with the theoretical prediction being 40% too low. The difference between the experiemtnal and calculated values is due to collisional deactivation which decreases the 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. We have shown that Stern-Volmer plots for the individual products can be constructed to determine the experiemtnal specific rate coefficients. The product ratios are independent of pressure in the range from 1 to 6 torr.

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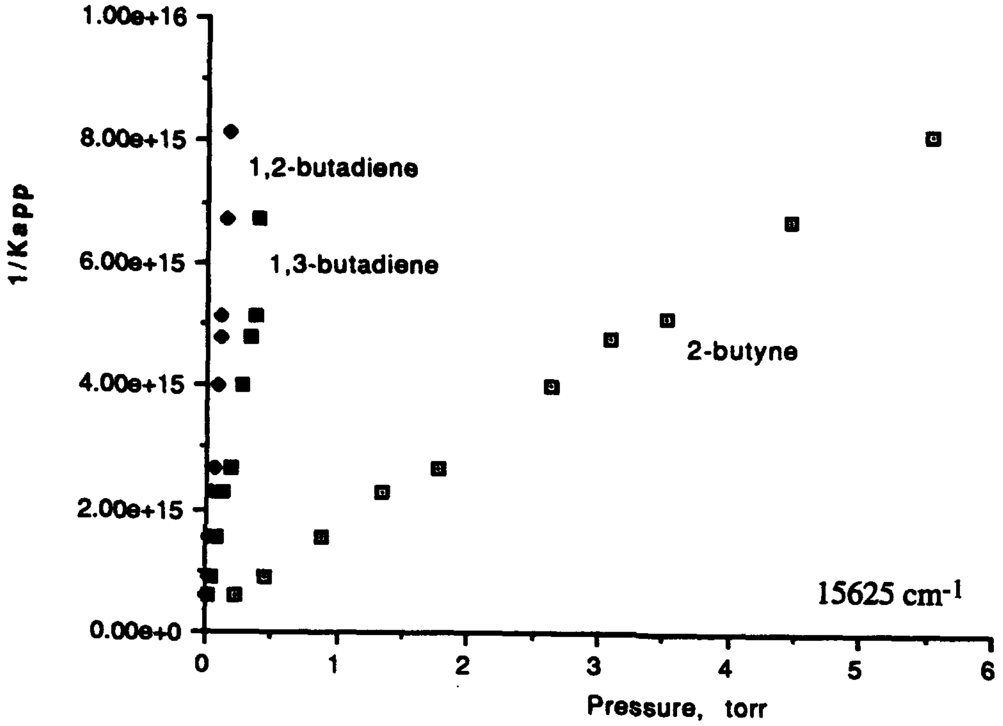

Figure 3 Stern-Volmer plot for the photolysis of the methylenic CH at 15623 cm^{-1}

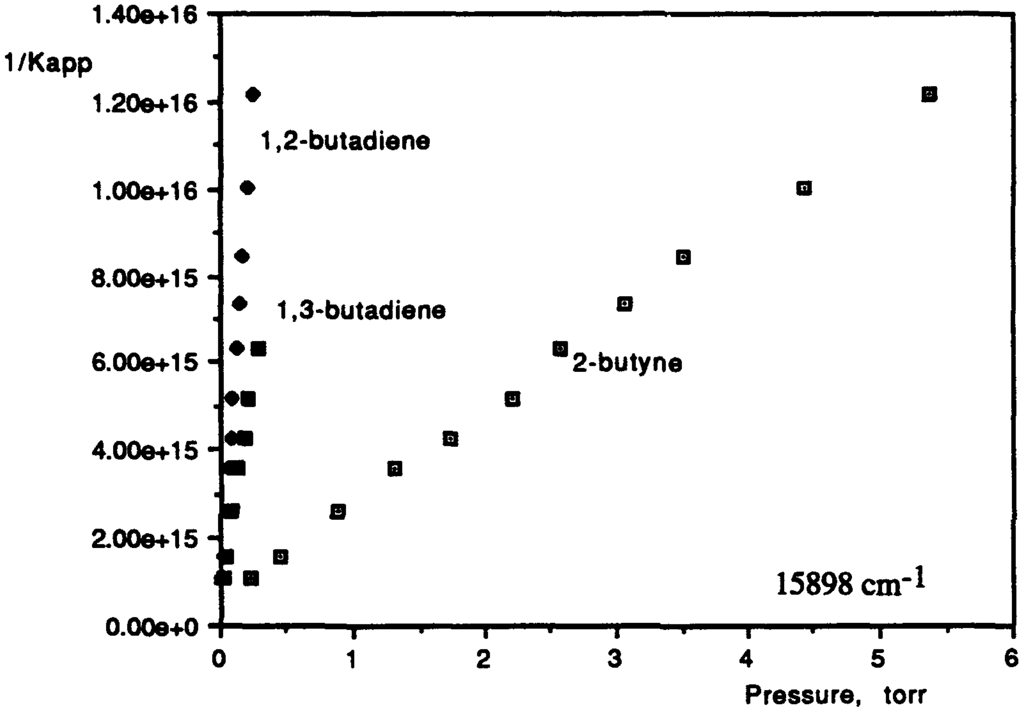

Figure 4 Stern-Volmer plot for the photolysis of the methyl in plane CH at 15898 cm^{-1}

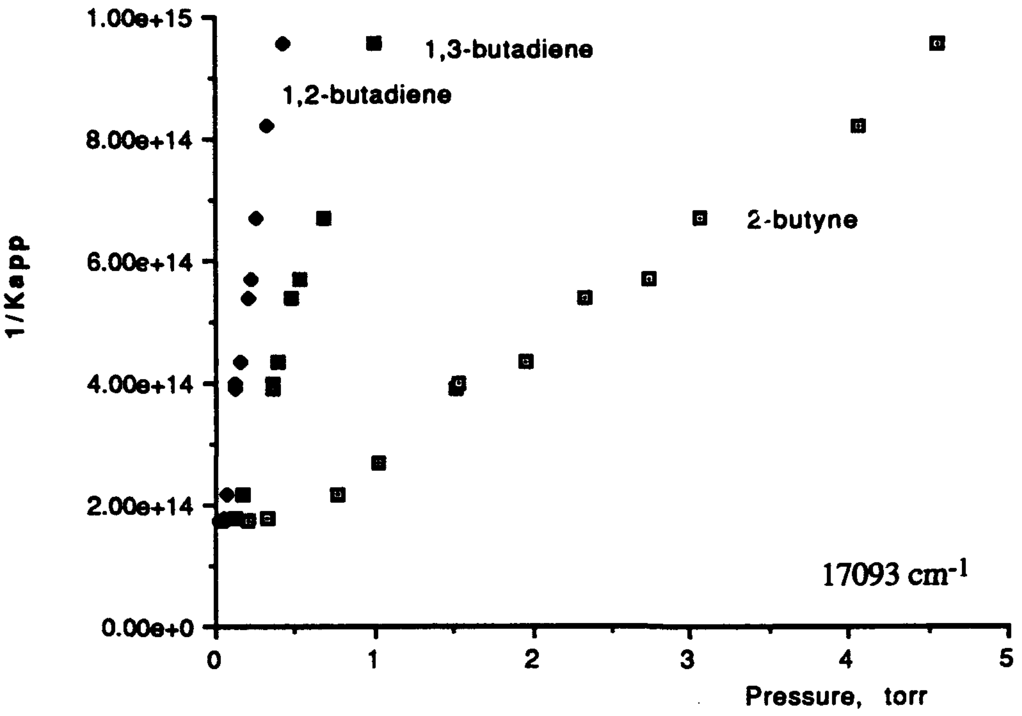

Figure 5 Stern-Volmer plot for the photolysis of the olefinic CH at 17093 cm^{-1}

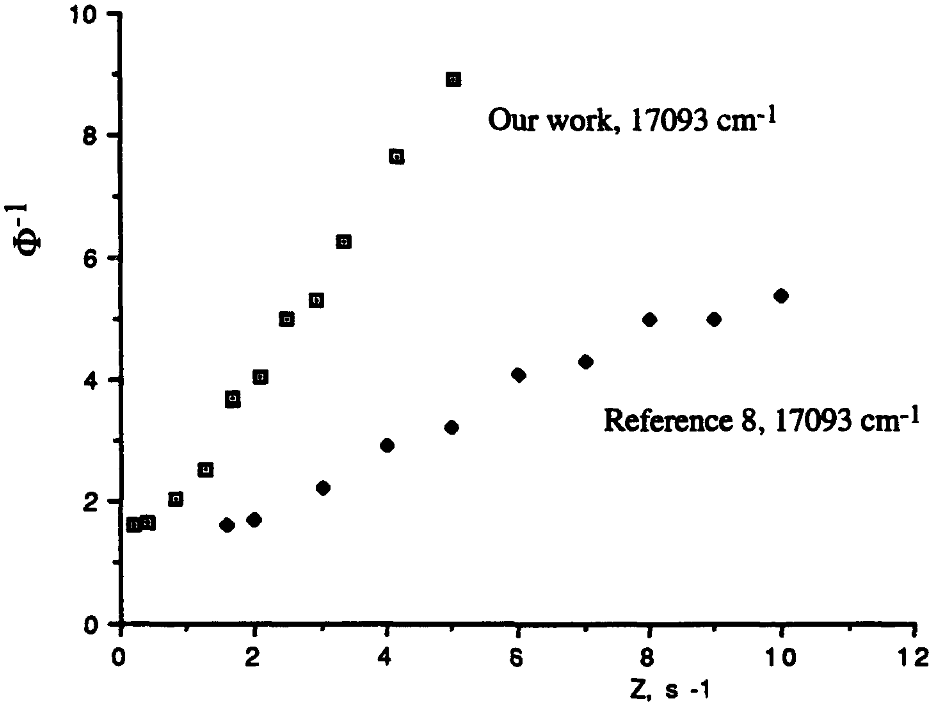

Figure 6 Comparison of the Stern-Volmer plot for the disappearence of methylcyclopropene from reference 3 and this work

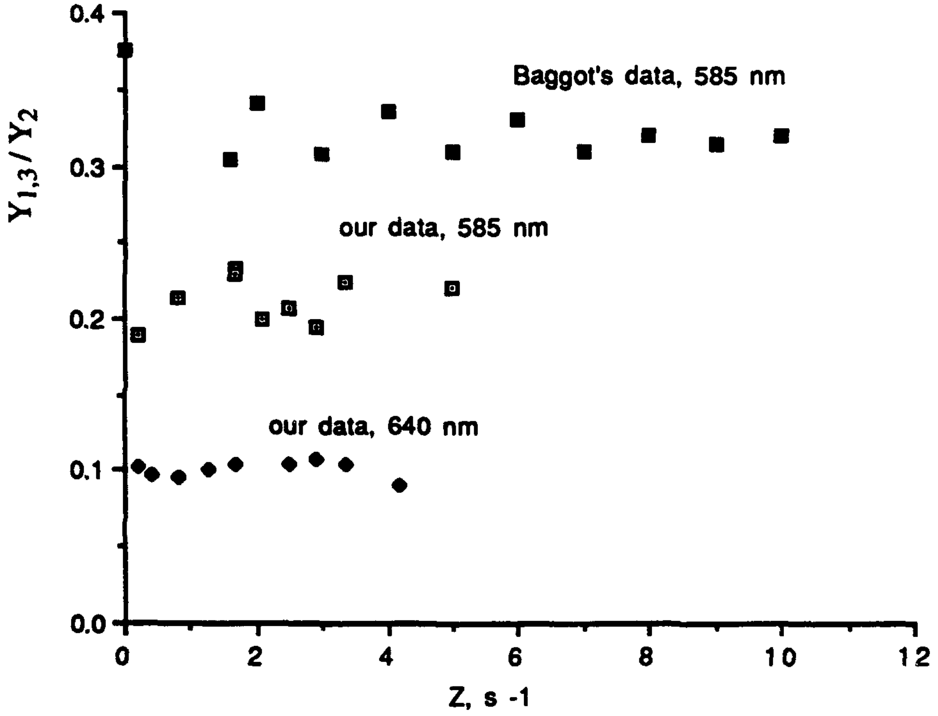

Figure 7 Product yield ratios Y_{13}/Y_2 for 1,3-butadiene and 2-butyne