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by

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## Photolysis within the absorption band contour for methyl isocyanide: vibrational overtone activation

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### Abstract

The photoisomerization of methyl isocyanide to form acetonitrile induced by excitation into the fourth (about 1kcal/mole above the activation barrier) and fifth (about 8kcal/mole above the barrier) C-H stretch vibrational overtone levels is reported. Four photolysis wavenumbers within the 5-0 band contour and three within the 6-0 contour were selected. The specific rate constant,  $k(E)$ , derived from Stern-Volmer plots with increasing excitation energies selected from across the rotational band contours, increase monotonically. The experimental  $k(E)$  agree with RRKM calculated values.

### Introduction

Recently, Segall and Zare<sup>1</sup> reported that the unimolecular specific rate for the photoisomerization of allyl isocyanide, excited to various wavelengths within the rotational band contour of the  $5\nu_{C-H}$  and  $6\nu_{C-H}$  overtone transitions, exhibits a nonmonotonic behavior with the excitation energy at room temperature. This was explained by a model which assumes an inhomogeneously broadened bandshape of the overtones by the presence of vibrational "hot bands". In this model, the molecules have different amounts of initial thermal energy across the overtone band. The "hot band" inhomogeneous broadening model precludes the possibility of nonstatistical effects which was indicated in previous work by Reddy and Berry<sup>2</sup>.

In allyl isocyanide there are three types of C-H oscillators giving rise to the overtone spectrum. These different C-H stretch overtone transitions overlap at each quantum level, consequently, the separation of vibrational contributions is difficult. Due to these complications any rotational effects could not be investigated. For methyl isocyanide, with only a single methyl C-H oscillator, the interpretation of the "hot band" model is simplified.

At room temperature the 5-0 and 6-0 C-H vibrational overtone transitions in gaseous methyl isocyanide are over  $100\text{ cm}^{-1}$  wide due to both homogeneous and inhomogeneous broadening. The absorption contours have contributions from both the rotational and vibrational absorptions, as well as homogeneous broadening. It has been shown in supersonic jets that the width of the band contour for small molecules ( $\text{H}_2\text{O}_2$ <sup>3</sup>,  $\text{H}_2\text{O}$ <sup>4</sup>,  $\text{CH}_4$ <sup>5</sup>) involves substantial inhomogeneous broadening. Methyl isocyanide possesses a low frequency bending mode which is populated at room temperature. This low frequency mode is envisioned as the reaction coordinate in the isomerization reaction to produce acetonitrile. The overtone absorption for molecules containing one quantum of bend will absorb on the red side of the

overtone feature due to anharmonicity. Thus photolysis on the red side of the 5-0 or 6-0 overtone transition might selectively excite molecules which already contain internal vibrational energy. Therefore, we have selected excitation wavelengths within the  $5\nu_{C-H}$  and  $6\nu_{C-H}$  overtone regions, in order to check the inhomogeneous broadening model. We found that the reaction rate increases monotonically with excitation energy and there is no contribution of "hot bands" to the photoisomerization reaction.

## Experimental

Methyl isocyanide (MIC) was synthesized by dehydration of N-methyl formamide <sup>6</sup>. Gas samples of MIC at known pressure (0.1- 160 Torr) were photolyzed inside the cavity of a cw dye laser, in a pyrex sample cell (22.5 cm length, 1.3 cm inside diameter) outfitted with two Brewsters angle quartz windows. In order to keep the product yield always around 2% so that absolute quantitative yields can be calculated, the samples were photolyzed for time periods ranging from 10 to 40 min depending on the sample pressure and photolysis wavelength. A Spectra Physics series 2000 argon ion laser was used to pump a Spectra Physics Model 375 B continuous wave broad band dye laser. The dye laser was tuned to the required wavelength using a motor driven three-plate birefringent filter with a resolution of about  $2\text{ cm}^{-1}$ . Rhodamine 6G and Pyridine 2 dyes were used in the dye laser for the 6-0 C-H (621.4 nm) and the 5-0 C-H (726.6 nm) overtones, respectively. Wavelengths were measured using Spex 1401 double monochromator. The model 815 power meter of Newport Corporation was used to monitor the output power of the dye laser during photolysis to ensure intracavity power stability. Sample pressures were measured using Datametrics Type 1400 electronic manometer with Type 590 series integral Barocel pressure transducer.

After photolysis, the product yield was measured with Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector and 3392A integrator. The sample components, methyl isocyanide and acetonitrile, were completely separated with a 12 ft x 1/8" stainless steel column packed with Chromosorb 104, 80/100 mesh (Alltech Associates). The column temperature maintained at 150 C with a He carrier gas flow rate of 30 ml/min. Retention times of 9 and 15 min were obtained for MIC and AN, respectively.

Methyl isocyanide sticks to all surfaces including the glass sample cell and the stainless steel sampling six-port valve and loop. In order to account for this process a careful analysis procedure was developed. The method of filling the photolysis cell and introducing the sample to the GC column was exactly reproduced for each experiment. The photolysis cell was filled with MIC (150 Torr) and "seasoned" for 5 days. MIC vapor was expanded from the liquid sample holder to the photolysis cell through the vacuum line to obtain a gas pressure around the desired pressure. The pressure final reading was taken after waiting 1/2 hour, when the change in the pressure become insignificant. The irradiated gas sample was then condensed onto the GC sampling loop by liquid nitrogen for 15 min, and injected cold into the column. This procedure (condensing and injection) was repeated at least two times until no more significant amount of the sample was detected. The sum of these three areas was used to calculate the percent product yield. The entire sample was condensed and injected if the pressure was lower than 40 Torr. In order to prevent saturating the GC column and detector, samples with higher pressures were expanded into the sampling loop for 5 min and only this expanded part ( $\sim 1/5$ ) was condensed and injected as before. The method was checked by injecting a known  $\sim 2\%$  gas mixture of AN in MIC at different pressures to give an error about 1%. Samples of

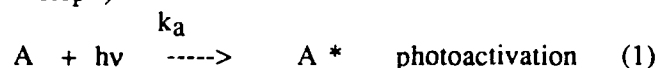
MIC diluted in Ar in a 1:25 ratio were prepared for each pressure directly in the photolysis cell: MIC vapor was first expanded into the photolysis cell as described before for pure MIC, then the Ar gas, which is stored in a sampling bulb connected to the vacuum line, was introduced to get the correct ratio at the specific pressure. By this we assure that the diluted mixtures have the same composition in the different pressures.

Some of the points were repeated 3 times in order to estimate the standard deviation. For the fourth overtone the typical error is about ~2% while for the fifth overtone is about ~3%. No dark reaction was observed for pure MIC and MIC in Ar without irradiation.

## Results and Discussion

### a : Stern-Volmer analysis

For the vibrational overtone activation experiment the Stern - Volmer treatment has been used repeatedly <sup>7</sup>. In the simple mechanism ( with only one reaction step ) :



a steady state concentration of the activated molecules  $A^*$  is assumed and the inverse apparent rate of reaction is plotted against the total pressure for a chosen excitation frequency according to the following equation

$$K_{ap}^{-1} [hv] = K_a^{-1} + K_d K(E)^{-1} K_a^{-1} [M]$$

where  $K_{ap}$  is the product apparent rate of reaction,  $K_a$  is the rate of photoactivation,  $K_d$  is the collisional deactivation rate constant,  $K(E)$  is the specific unimolecular rate constant and  $[hn]$  is the intracavity photon number density. In the simple " strong collider approximation " the Stern-Volmer plot should be a straight line for all pressure regions. The slope of this line yields the ratio of the collisional deactivation rate to the specific rate constant,  $K_d / K(E)$ , while from the intercept, the photoactivation rate  $K_a$  can be obtained.  $K_a$  can be calculated independently by the equation

$$K_a = \sigma(n)c$$

where  $\sigma(n)$  is the absorption cross section at the photolysis frequency and  $c$  is the speed of light. The photon number density is determined at each wavelength using the relation

$$[hv] = 2 (5.04 \times 10^{14}) l p / c T A_{eff}$$

where  $l$  is the photolysis wavelength in  $\text{\AA}$ ,  $T$  is the transmittance of the dye laser end mirror at the photolysis wavelength,  $c$  is the speed of light,  $A_{eff}$  is the effective cross

sectional area in  $\text{cm}^2$  of the cell defined as the cell volume divided by the cell length, and  $p$  is the extracavity power during photolysis <sup>8</sup>.

### b. Photoisomerization results

The photolysis wavenumbers chosen for investigation are shown in Figure 1. Four photolysis wavenumbers within the 5-0 band contour and three within the 6-0 contour were selected. The 5-0 transition peak maximum occurs at  $13,763 \text{ cm}^{-1}$ . We photolyzed on this peak,  $25 \text{ cm}^{-1}$  to the red and  $25 \text{ cm}^{-1}$  to the blue. Because the 5-0 contour is not symmetric we chose one additional wavenumber shifted  $158 \text{ cm}^{-1}$  to the red. The 6-0 transition maximum occurs at  $16088 \text{ cm}^{-1}$ . We photolyzed on the peak and  $100 \text{ cm}^{-1}$  to the red and the blue.

Figures 2 and 3 show Stern-Volmer plots for the photolysis of pure MIC and MIC diluted in argon at several wavelengths selected from across the  $5\nu_{C-H}$  and  $6\nu_{C-H}$  regions, respectively. Only data above 10 and 40 Torr were considered in fitting the  $5\nu_{C-H}$  and  $6\nu_{C-H}$  overtone regions, respectively. The extrapolated intercepts for these plots approximately followed the change in absorption intensity at the different wavelengths across the rotational band contours. Table I gives the absorption cross sections obtained from our experimental Stern-Volmer intercepts and the measured spectroscopic cross sections (taken from reference 9). The cross section values we obtained are about a factor of two higher but the ratios of the cross sections for the different wavelengths are still the same.

Table I : Absorption cross sections from the  $5\nu_{C-H}$  and  $6\nu_{C-H}$  overtone region of MIC .

overtone transition	$\nu$ ( $\text{cm}^{-1}$ )	$\sigma$ (mbn) <sup>a</sup>	$\sigma$ (mbn) <sup>b</sup>
5-0 (MIC-MIC)	13605	1013	550
	13738	2148	1168
	13763	2215	1200
	13788	1542	758
5-0 (MIC-Ar)	13738	2212	
	13763	2284	
	13788	1555	
6-0 (MIC-MIC)	15988	227	55
	16088	517	120
	16188	230	55
6-0 (MIC-Ar)	16088	447	

a Cross sections from Stern-Volmer intercepts

b Spectroscopic cross sections taken from reference 9

The specific rate,  $K(E)$ , values obtained from the slopes and extrapolated high-pressure intercepts, using linear regression fits to the experimental data, are

tabulated in Table II. In order to determine the  $K(E)$ , the value of  $K_d$  must be calculated using either the hard sphere, Lennard-Jones or Stockmayer collision model. The Stockmayer potential collision parameters (appropriate for polar collision partners) were used in this work. For MIC-MIC, the collision frequency is  $1.99 \times 10^7 \text{ Torr}^{-1} \text{ sec}^{-1}$  and for MIC-Ar is  $9.58 \times 10^6 \text{ Torr}^{-1} \text{ sec}^{-1}$  as obtained in reference 7. In every case,  $K(E)$  increases monotonically with increasing excitation energy even within the individual band contours.

Table II : Specific reaction rate constants derived from the experimental Stern-Volmer photoysis plots at different excitation energies.

overtone transition	$\nu$ ( $\text{cm}^{-1}$ )	collider gas	$K(E) \text{ sec}^{-1}$
5-0	13605	MIC	$2.848 \times 10^8 \pm (0.057 \times 10^8)$
	13738		$3.868 \times 10^8 \pm (0.077 \times 10^8)$
	13763		$3.943 \times 10^8 \pm (0.079 \times 10^8)$
	13788		$4.093 \times 10^8 \pm (0.082 \times 10^8)$
6-0	15988	MIC	$5.011 \times 10^9 \pm (0.15 \times 10^9)$
	16088		$5.712 \times 10^9 \pm (0.11 \times 10^9)$
	16188		$6.594 \times 10^9 \pm (0.20 \times 10^9)$

### c. Overtone transition broadening mechanism:

Figure 4 presents the RRKM plot of the calculated  $K(E)$  along with the experimental values obtained for MIC in both overtone transitions. The Hase-Bunker RRKM program <sup>10</sup> was used for the calculation with the following options: 1) adiabatic rotations and harmonic vibrations, 2) direct counting for the sum of states in the critical configuration and semiclassical counting in the reactant, 3) prescribed critical configuration, and 4) a reaction path degeneracy of 3 and a critical energy of 37.85 kcal/mole, as given in reference <sup>11</sup>. The vibrational and rotational parameters of the "300 model" for MIC suggested by Rabinovitch <sup>11</sup> were used. As can be seen from Table II, the experimental  $K(E)$  agree with the calculated values, and increase with increasing excitation energy. This behavior is in contrast to the previous results obtained for allyl isocyanide <sup>1</sup> indicating that the thermal effect ("hot" bands and rotational effects) has little contribution to the width of the overtone features in MIC, and the dominant contribution is homogeneous. However, a low temperature spectrum of the overtone transitions is still needed to confirm the above conclusion.

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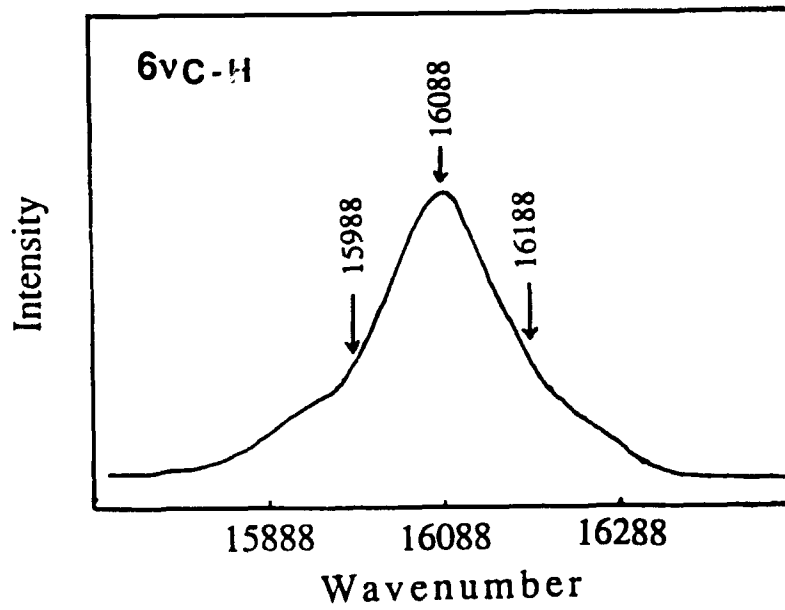
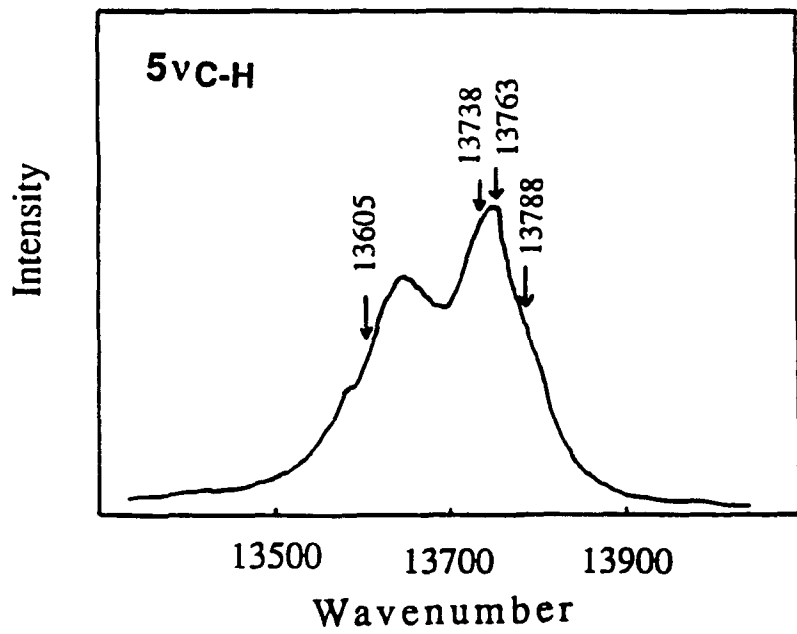


Figure 1

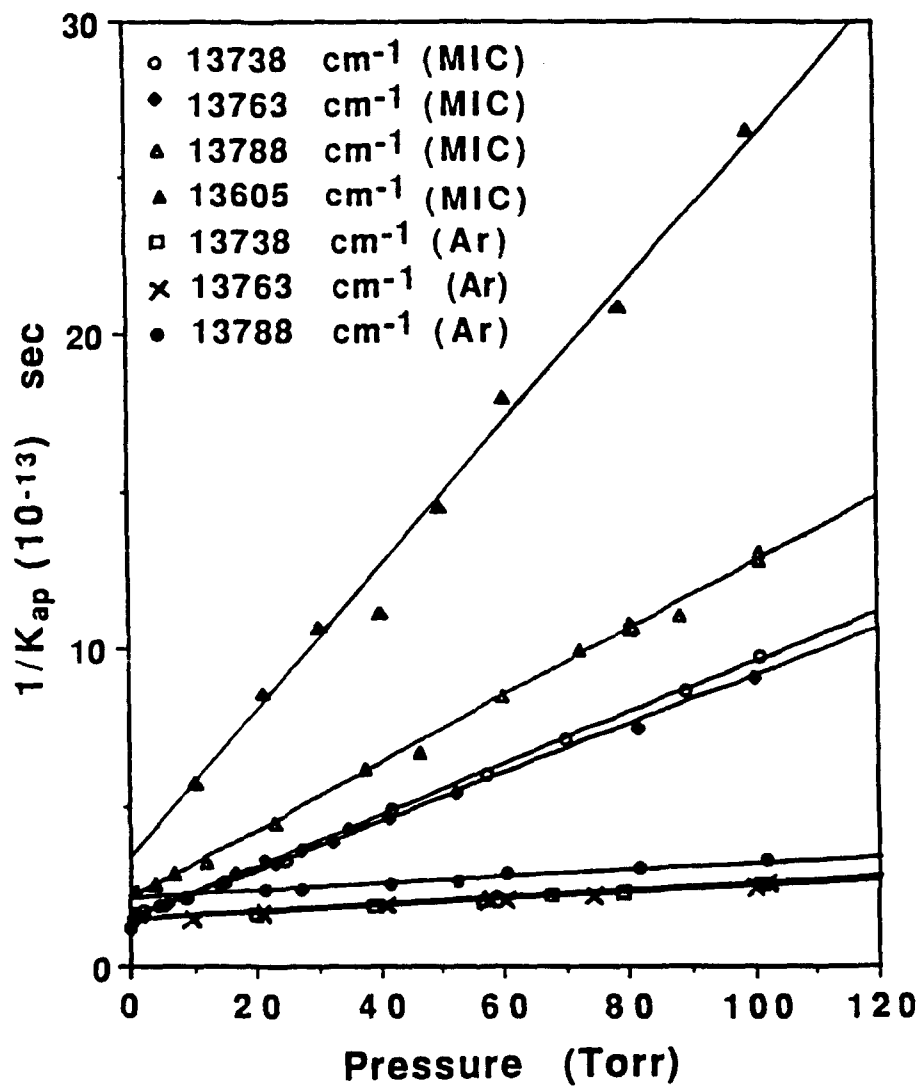


Figure 2

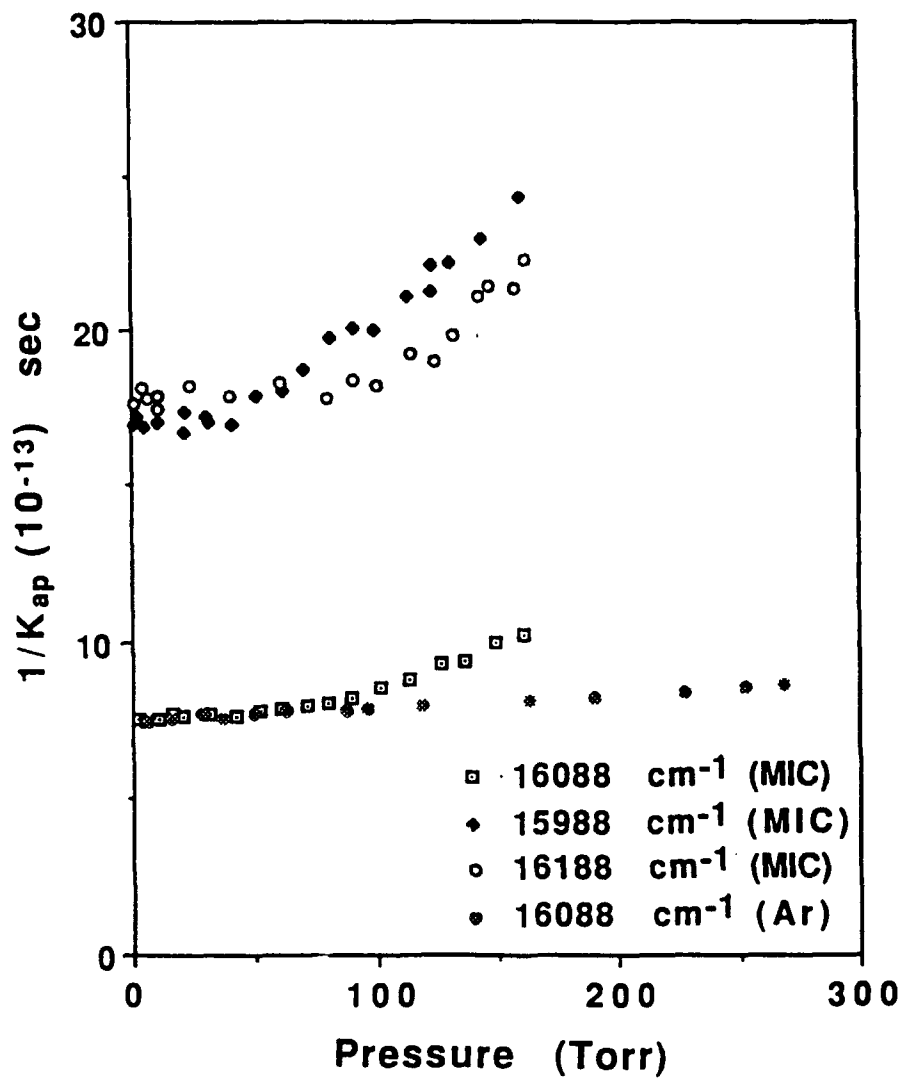


Figure 3

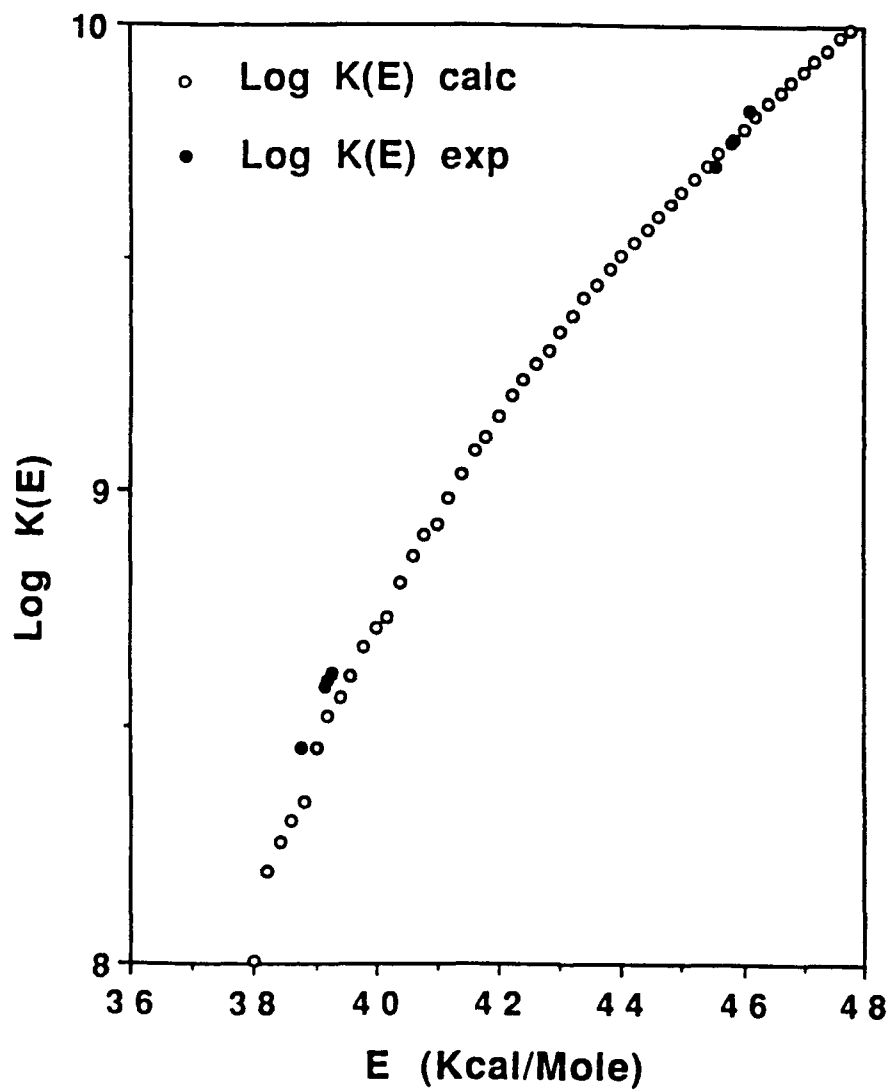


Figure 4