HOW EFFECTIVE IS INTERNAL EXCITATION IN PROMOTING THE HCl+1,3-BUTADIENE ADDITION REACTION?

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Excitation of the C–H overtones of 1,3-butadiene in the presence of HCl to an energy ≈ 16 kcal mol^{-1} in excess of the activation energy causes the formation of no detectable addition products. This indicates that the rate constant for the formation of 1-chloro-2-butene is at least slower than 2.1×10^{-14} cm^3 $molecule^{-1}$ s^{-1}.

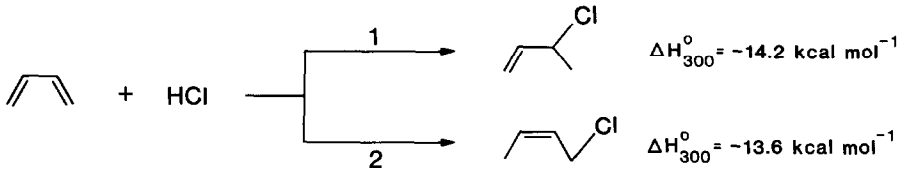
1. Introduction

The effects of vibrational excitation on the rates of bimolecular reactions are of considerable interest because of the possibility of enhancing reaction rates. This reaction rate enhancement results either from putting additional energy in the system and hence lowering the effective barrier to reaction, or from dynamical considerations [1]. To date both experimental and theoretical studies have largely concentrated on A+BC→AB+C atom transfer reactions. In fact there have been few studies of vibrational enhancement in bimolecular reactions involving stable molecular species [2–5].

The addition of HCl to 1,3-butadiene has been studied previously. Herman and Marling [3] pumped the HCl vibration in an attempt to promote the addition reaction, but they failed to observe laser-induced products. In this study we directly pump overtones of the C–H stretch in 1,3-butadiene. A visible dye laser produces vibrationally excited molecules with well-defined internal energies in excess of the activation energy. In the absence of dynamical effects vibrational excitation of 1,3-butadiene should be as efficient as vibrational excitation of hydrogen chloride in promoting the reaction for a given total energy. (The validity of this statement will be discussed later.) There are also experimental advantages in pumping C–H stretches. The peak cross sections are nearly two orders of magnitude larger than those for HCl and are also pressure independent. Since the ratio of reactive to non-reactive collisions is also constant, it is possible to perform experiments at high pressures, where the collision rate is higher, to increase the amount of products formed for a given photolysis time.

The reaction under study can proceed via two exothermic channels (see scheme 1). Channel 1 corresponds to a four-center Markownikoff transition state. The A factor for this channel is 1×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and the activation energy is 33 ± 2 kcal mol^{-1} [6,7]. Channel 2 corresponds to a six-center Markownikoff transition state. The A factor is 1.7×10^{-13} cm^3 $molecule^{-1}$ s^{-1} [8] ‡ and the acti-

‡ Computed from the A factor for the reverse unimolecular reaction of ref. [8].



Scheme 1.

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vation energy is 29 ± 2 kcal mol^{-1} [3]. The 1,3-butadiene + HCl reaction was chosen because of the high A factor for channel 1, the high vapor pressure of 1,3-butadiene at room temperature (2.4 atm), and the relatively low activation energies for both channels. These factors make this reaction a favorable candidate for overtone chemistry.

2. Experimental

The experimental apparatus has been described previously [9] and will only be outlined here. The vibrationally excited 1,3-butadiene was formed using intracavity overtone absorption by placing a photolysis cell in the cavity of a linear dye laser. The dye laser was tuned to the C–H overtone feature of interest by rotating a two-plate birefringent filter (resolution 3 cm^{-1}), placed at Brewster's angle in the dye cavity, using the opto-acoustic signal from a resonance cell containing 1,3-butadiene. Intracavity powers were measured by monitoring the output power from the dye laser using an NRC 815 power meter. Oxazine perchlorate dye pumped by a krypton ion laser was used and the intracavity power was 25–35 W with the photolysis cell in the cavity.

Fig. 1 shows the opto-acoustic spectrum of the 5–0 C–H overtone features. The peak assignments are based on ref. [9]. The absolute peak cross sections

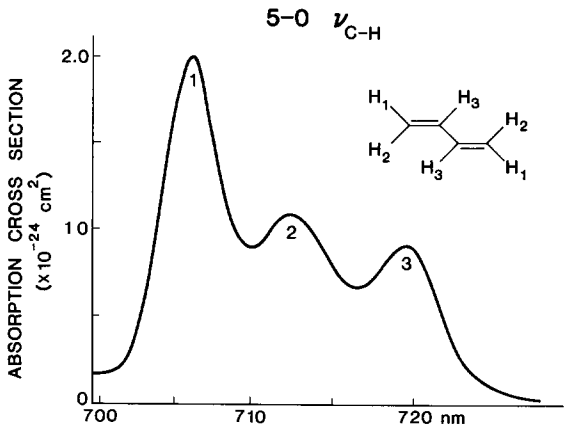

Fig. 1. The 5–0 C–H overtone absorption opto-acoustic spectrum of 1,3-butadiene. Peaks 1, 2 and 3 correspond to the absorptions from the three types of H atoms labeled on the structure shown.

were measured by recording opto-acoustic spectra of mixtures of 1,3-butadiene and neopentane and also neopentane and benzene [9].

The quantitative analysis of both products was performed using a Perkin–Elmer 3920 GC with a FID detector. A 6 ft. stainless steel column packed with 0.19% picric acid on graphpac GC 80/100 was used. Retention times were determined using commercially available products. The reagents were supplied by Matheson. The HCl was 99.995% pure and the 1,3-butadiene was 99.5% pure (the impurities being 0.2% 1-butene, 0.1% trans-2-butene, 0.05% isobutylene, and 0.005% butadiene dimer).

Preliminary experiments indicated that there was a surface catalyzed "dark" reaction. This was found to be independent of lighting conditions, to be approximately proportional to the pressure of HCl and the pressure of 1,3-butadiene and to take place on the quartz walls and windows of the photolysis cell. This surface reaction was greatly reduced by coating the cell walls with halocarbon wax or using teflon cells. The photolysis cell used in all experiments had a teflon stopcock and walls coated with halocarbon wax. It was 6 in. long and had an inside diameter of 0.23 in. The quartz windows were attached at Brewster's angle using Torr–Seal (Varian). The experiments were all performed at room temperature with 380 Torr of each reagent. Null runs with the laser on and off were performed immediately before or after the laser runs. The detection sensitivity was such that a yield of 0.002% of addition products could readily be detected.

3. Results

Table 1 summarizes the experimental results. There is essentially no difference observed in product yields with the laser on and laser off. The laser on and off runs were averaged for each experiment and are shown in the last column. Note that the scatter for all three data sets is ± 0.03–0.04%, although there is some variation in the average value. These experiments show that if a laser-induced reaction had occurred, a yield of 0.08% or greater could have been detected.

Table 1
Results of the vibrationally excited 1,3-butadiene plus HCl addition reaction experiments. The yields are fractional conversions in percent. Pairs of runs are shown for the laser on and the laser off. The yield of 1-chloro-2-butene is directly below the yield of 2-chloro-3-butene for the same run

C–H overtone feature pumped	Products	Photolysis time (h)	Laser on yield (%)		Laser off yield (%)		Average yield (%)
1	2-chloro-3-butene	12	0.13	0.16	0.18	0.16	0.16±0.03
	1-chloro-2-butene		0.18	0.21	0.29	0.21	0.22±0.04
2	2-chloro-3-butene	10¼	0.20	0.21	0.24	0.17	0.21±0.03
	1-chloro-2-butene		0.27	0.27	0.32	0.24	0.28±0.03
3	2-chloro-3-butene	10	0.24	0.19	0.20	0.30	0.23±0.04
	1-chloro-2-butene		0.40	0.32	0.38	0.40	0.38±0.03

4. Discussion

The overall rate of formation of addition products is obtained by assuming that the vibrationally excited 1,3-butadiene has a steady state concentration:

$$\frac{\mathrm{d[product]}}{\mathrm{d}t} = \frac{\sigma_B P}{A_{cell}\hbar\omega} k_R \frac{[\mathrm{HCl}][1,3\text{-but}]}{\gamma[1,3\text{-but}] + (\gamma' + k_R)[\mathrm{HCl}]}, \quad (1)$$

where A_{cell} is the cross-sectional area of the cell, σ_B the peak absorption cross section of the 1,3-butadiene C–H stretch, P the intracavity power, $\hbar\omega$ the photon energy, γ and γ' are the rate constants for vibrational relaxation of vibrationally excited 1,3-butadiene by 1,3-butadiene and HCl, respectively, and k_R is the overall rate constant for the addition reaction of 1,3-butadiene having internal energy $\hbar\omega$ with HCl.

Note that for a fixed composition the rate of formation of products is proportional to the total pressure since σ_B is pressure independent for the broad (≈ 100 cm^{-1}) C–H overtone features. Thus it is advantageous to work at high pressures for experiments involving the vibrational excitation of 1,3-butadiene. In contrast, if the HCl is pumped with a laser narrower than the Doppler width, then at total pressures above 50 Torr, σ_{HCl} becomes proportional to $1/P_{total}$ due to pressure broadening. Consequently there is no advantage in working at total pressures above 50 Torr when HCl overtones are pumped.

Assuming γ and γ' are gas kinetic (strong collision approximation), it is possible to calculate an upper limit for k_R since all other parameters in eq. (1) are known. (The strong collision approximation is unlikely to be valid for such high energies and the data will be corrected for this later.) The overall rate constant for addition of 1,3-butadiene with 40 kcal mol^{-1} of internal energy to HCl is less than 4.1×10^{-14} cm^3 molecule^{-1} s^{-1}.

For comparison a statistical bimolecular rate was also calculated by performing an RRKM calculation for the reverse unimolecular decomposition and then using the principle of microscopic reversibility to obtain the bimolecular rate:

$$k_{bi}(E) = k_{uni}(E) \frac{\rho_{adduct}(E)}{\rho_{HCl}(E)\,\rho_{butadiene}(E)}, \quad (2)$$

where $k_{uni}(E)$ and $k_{bi}(E)$ are the rate constants for the unimolecular and bimolecular reactions, respectively, at total energy E. $\rho_{adduct}(E)$, $\rho_{HCl}(E)$ and $\rho_{butadiene}(E)$ are the densities of states for the adduct, HCl and 1,3-butadiene, respectively.

The $k(E)$ values for each channel were obtained from a standard RRKM calculation. For both calculations it was assumed that $I^\dagger/I = 1$. The A factors for the reactions and the frequencies used for the molecules and complexes are shown in table 2. The transition state for the four-center elimination was based on that used for $C_4H_8Cl_2$ by Setser and co-workers [10]. The frequencies of the transition state for six-center elimination were adjusted to agree with the high-pressure A factor. The densities of states were calculated as in ref. [11].

Fig. 2 shows the results for this calculation. Note that the reaction does not proceed with a rate constant of the A factor above the barrier, as one might

Table 2
RRKM calculation parameters

Vibrational frequencies (cm^{-1})			
1-chloro-2-butene [a]		2-chloro-3-butene [b]	
molecule	complex	molecule	complex
2933(7), 1661, 1449(3), 1369, 1319, 1302, 1291, 1234, 1198, 1107, 1051, 932, 875, 811, 746, 653, 474, 302, 265, 107, 90	2933(7), 1661, 1449(3), 1369, 1319, 1302, 1291, 1234, 1198, 1107, 1051, 932, 875, 811, 746, 524, 410, 400, 250(2)	2933(7), 1661, 1449(4), 1315(3), 1247(3), 1062(4), 918, 734(2), 353, 160, 105, 81(2)	3010(6), 1661, 1363(4), 1294, 1093(3), 927(5), 830(2), 664, 537(2), 400, 200, 105, 81

[a] A factor: 10^{12} s^{-1} [6]. [b] A factor: 2.2×10^{13} s^{-1} [8].

naively think. The rate constant only approaches the A factor at large energies above the barrier. The experiment was conducted at a total energy of 16000 cm^{-1} including the thermal energy of the reagents. The predicted rate constant for production of both products at total energy 16000 cm^{-1} was found from

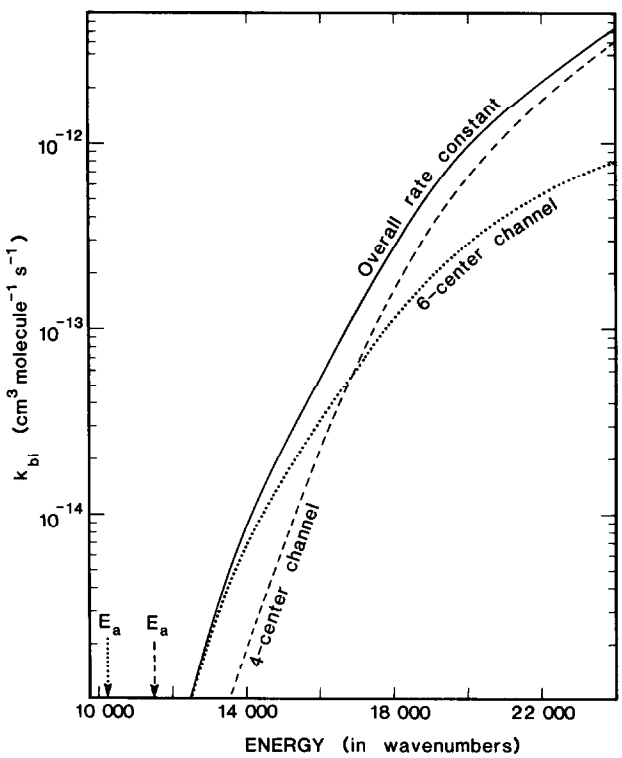

Fig. 2. Calculated specific rate constants for the bimolecular addition reaction of 1,3-butadiene with HCl, based on eq. (2).

the curve and was then corrected for collisional relaxation assuming the adduct loses 1000 cm^{-1} per collision. The value obtained was 9.2×10^{-14} cm^3 $molecule^{-1}$ s^{-1} and two collisions on average are required to remove the excess energy. The experimental results were corrected for a collisional relaxation rate which was half gas kinetic and the overall rate constant is less than 2.1×10^{-14} cm^3 $molecule^{-1}$ s^{-1} with 40 kcal mol^{-1} of internal energy in the 1,3-butadiene. This is at least four times slower than the statistical rate at a total energy of 16000 cm^{-1}. Hence our negative observation of the formation of addition product via overtone pumping of 1,3-butadiene may offer insight nevertheless into the dynamics of this reaction.

Let us consider the alternative experiment of pumping the HCl overtones which has been performed previously by Herman and Marling. We reanalyzed their data, since the relaxation rate constants for HCl ($v=5$) and HCl ($v=6$) with hydrocarbons have been shown to be gas kinetic [12] and the absorption cross sections have been measured [13]. For both HCl ($v=5$) and HCl ($v=6$) the overall rate constant is less than 6.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Hence the pumping of HCl overtones is a less sensitive experiment than the present one by three orders of magnitude.

Considering the unimolecular decomposition, it is expected that the energy in excess of the barrier (16 kcal mol^{-1} in this case) will be distributed statistically among the product states. In contrast, the distribution of the barrier energy (29 kcal mol^{-1}) will be highly dependent on the nature of the exit channel barrier and this will largely determine how effective

internal excitation of 1,3-butadiene is at overcoming the barrier for the reverse addition reaction. To our knowledge there have been no studies on energy disposal in six-center elimination reactions. For four-center elimination reactions of chloroethanes, Lee and co-workers [14] found only 20% of the exit channel barrier energy goes into translation. Berry [15] found, again for chloroethanes, that about 10% of the total available energy goes into vibrational excitation of the HCl. It is difficult to extrapolate such limited data to six-center or four-center elimination reactions of chlorobutenes. In the absence of additional data it is only possible to compare our experimental data with the statistical calculation. Furthermore, the limited studies on four-center elimination reactions suggest that while energy disposal is not statistical, the post barrier interaction is sufficiently strong to couple translational and internal motions with high efficiency.

We interpret our results as indicating that:

(1) Internal excitation of the 1,3-butadiene, on its own, is inefficient at overcoming the barrier, and

(2) Vibrational excitation of the HCl or relative translation of the reagents or both are also required to promote the addition reaction.

These conclusions are very similar to the results of the trajectory calculations of Polanyi and co-workers [16] on the much simpler atom-plus-diatom exchange reactions, $A+BC \rightarrow AB+C$. It was found that for exoergic reactions, relative translation is particularly effective in promoting reaction. This is a consequence of the potential-energy surface generally having an early barrier which is surmounted more effectively by translation than by reagent vibration. The system we have studied is more complicated, involving a multidimensional vibration. The system we have studied is more complicated, involving a multidimensional potential hypersurface; nevertheless the same conclusion seems valid. The question remains whether this result is general.

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