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Vibrationally stimulated addition reactions between hydrogen halides and unsaturated hydrocarbons: A negative result[a)]

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No evidence for enhancement of gas phase addition reactions between hydrogen halides and unsaturated hydrocarbons was observed in cases where one reactant was prepared in a high vibrational state by laser excitation of an overtone transition. The specific reaction systems studied were $HCl(v = 5 \text{ or } 6) +$ various unsaturated hydrocarbons, and also $C_2H_2(00500) +$ HBr or HCl, at room temperature. The reactant states were prepared by one photon-overtone absorption inside a cw dye laser, to an energy level above the activation energy of the corresponding thermal reaction. It is estimated that the rate constant for addition of these vibrationally excited molecules is at least 10–1000 times slower than the rate corresponding to the pre-exponential factor of the associated thermal reaction, depending on the employed rate of collisional quenching. Also, the reaction of $C_2H_2(00500) +$ HBr did not appear to accelerate even when heated to 300°C.

I. INTRODUCTION

In recent years, there has been increasing interest in measuring and predicting the specificity of vibrational and translational energy consumption in gas-phase bimolecular reactions. Most theoretical and experimental effort has been focused on examples of the $A + BC \rightarrow AB + C$ atom transfer reaction[1]; however, bimolecular reactions between larger, vibrationally excited reagents have also been studied, but to a lesser degree. Notable among these investigations are the studies of the O-atom transfer reaction $NO + O_3 \rightarrow NO_2[X(^2A_1) \text{ or } ^2B_2] + O_2$ in which either reactant has been vibrationally excited.[2] Though most of the studies reported in the literature have centered on these atom transfer reactions, there have been a few exceptions, such as the study of the (supposedly) 4-centered exchange (metathesis) reaction: $H_2(v \geq 4) + D_2 \rightarrow 2HD$.[3] This paper reports on an attempt to observe molecular addition reactions in which one of the reactants is vibrationally excited by one-photon, overtone absorption in a dye laser to an energy level lying above the activation energy of the corresponding thermal reaction. Specifically, the addition of $HCl(v = 5, 6)$ to various simple and conjugated alkenes and of HBr and HCl to $C_2H_2(00500)$ were investigated.

Benson and co-workers,[4] Kubota,[5] and Gorton and Walsh,[6] among others, have experimentally studied the gas phase thermal addition of HI to various alkenes. The observed reactions were found to be homogeneous, and bimolecular, with radicals playing no noticeable role in many of these reactions. Thermal addition of the lighter hydrogen halides to olefins has not been observed simply because the formed products decompose at the temperatures required for measurable forward reaction.[4] Two types of transition states have been hypothesized for these reactions: (1) a 4-centered activated complex with the hydrogen halide (HX) centered across a double or triple bond, and (2) a 6-centered transition state of HX across a -diene group ($-C{=}C-C{=}C-$).[6] Arrhenius pre-exponential factors and activation energies for these reactions can be determined from the rate of the reverse decomposition reactions or may instead be estimated using the semi-ion model of Benson and Bose.[7,8] Similar addition reactions have also been induced by electronic excitation of a reactant. One example is the isotopically selective addition: $ICl^* + C_2H_2$ by Stuke and Schafer.[9]

The main consequences of these addition reactions are the breaking of the H–X and a C–C bond and the subsequent increase of the H–X and C–C bond distances in the newly formed addition product. Therefore, the wave function overlap of reactant states with the transition states and the product states should increase if the HX vibrational mode and/or the C–C stretching mode are excited; the reaction cross section should increase accordingly. This supposition is strengthened by the appearance of more than the statistical share of available energy in HX product vibration determined in studies of the reverse reaction, that is, 4-centered ($\alpha\beta$) dehydrohalogenation. Berry[10] estimates that in these reactions ~15%–40% of the available energy is partitioned to the HX elimination product vibrational mode. This appears to be true, independent of the method of halocarbon excitation, be it chemical activation, ultraviolet absorption, or infrared multiple-photon absorption, as discussed in the reviews by Berry[10] and Bauer.[11] Two of these studies which are relevant to this report are the CO_2 laser photolyses by Quick and Wittig in C_2H_3F,[12] and West *et al.* in CF_3CH_3 and CF_2ClCH_3.[13] In agreement with the above discussion, the HX products in both studies were formed in vibrationally excited states, as monitored by fluorescence detection. Furthermore, West *et al.* have also observed fluorescence at the C–H stretching frequency in CF_3CH_3 photolysis which is apparently from the CF_2CH_2 product. In apparent contradiction to this, Quick and Wittig claim that the C–H stretching mode in the C_2H_2 product is unexcited in their study.

Microscopic reversibility assures only that the rates of addition reactions can definitely be enhanced if the reactants are prepared in the quantum states of the nascent products of the associated decomposition reaction (with velocity reversed). If sufficient vibrational

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TABLE I. Addition reaction reagents.

Reactant pair	Products	Frequency factor (log$A$, 1/mole-sec)	Activation energy[c] (kcal/mole)	ΔH(300 °K)[f] (kcal/mole)
HCl +				
1) C_2Cl_4	$[C_2HO]_5$	~8.3[a]	35.5[d]	-14.0
2) 1,3-butadiene	3-chloro-1-butene	~8.0[a]	~33.0[a]	-14.2
	4-chloro-2-butene	8.8[a]	29.0[a]	-13.6
3) 2-methyl-1,3-butadiene	1-chloro-3-methyl-2-butene	8.4[a]	26.0[a]	-13.9
4) 1,3-cyclohexadiene	3-chlorocyclohexene	~8.0[b]	20–25[b]	-14.7
C_2H_2 +				
5) HBr	C_2H_3Br	8.3[a]	33.3[e]	-28.2
6) HCl	C_2H_3Cl	8.3[a]	36.4[e]	-27.1

[a] Reference 14.
[b] Estimated value.
[c] All quoted values of the activation energy are ±2 kcal/mole.
[d] Reference 7(d).
[e] Reference 7(c).
[f] Reference 8.

energy is deposited into a single specific mode of one of the reactants, it is possible, though not certain, that the reaction will occur without need for an accompanying increase in relative translational energy or excitation of other vibrational modes. This required amount of energy may in fact be much larger than the thermal activation energy, which is itself approximately equal to the height of the reaction barrier, if it is $\gg kT$ (as it is in the reactions under scrutiny).

The isotopically selective vibrationally enhanced $DX^{\dagger}$ + olefin addition reaction has been suggested a possible means of deuterium isotope separation by Marling *et al.*[14] The idea of laser-induced $HX^{\dagger}$–olefin addition reactions has also been considered in various contexts by Szoke,[15] Berry,[16] and Bauer.[17]

II. EXPERIMENTAL TECHNIQUE

The addition of vibrationally excited HCl to various unsaturated molecules and of HBr or HCl to vibrationally excited acetylene was investigated in this study. Table I lists the various reactant pairs examined with the anticipated products, as well as the estimated pre-exponential factors, activation energies and enthalpy changes for the associated thermal reactions.

The vibrationally excited species were prepared by single photon, CW dye laser intracavity overtone absorption with the experimental arrangement diagrammed in Fig. 1. This apparatus was similar to that employed by Berry and co-workers.[18] The output mirror was extended outside the chassis of the employed commercial dye laser to permit insertion of a reaction cell and a molecular resonance detection cell inside the laser cavity. Laser oscillation was limited to one or two longitudinal modes by using 1 mm and 5 mm thick uncoated quartz etalons as frequency-selective elements in addition to a 3-plate birefringent filter.

HCl was excited to $v = 5$ (7440 Å, 38.3 kcal/mole) using the Oxazine-1 perchlorate dye pumped by a krypton ion laser while HCl($v = 6$) (6320 Å, 45.1 kcal/mole) was prepared in a Kiton-Red S CW dye laser pumped by an argon-ion laser. The matrix elements of these weak transitions have been calculated to be -4.5×10^{-23} esu-cm ($5 \leftarrow 0$) and $+2.3\times10^{-23}$ esu-cm ($6 \leftarrow 0$).[19] Based on these matrix elements, the absorption coefficients for fully Doppler broadened $H^{35}Cl$-R(2) transitions in a normal isotopic mixture of HCl are 4.7×10^{-6} and 1.2×10^{-6}/torr-cm, respectively. C_2H_2 was pumped to (00500) (6400 Å, 44.6 kcal/mole),[20] that is, the fourth overtone of the ν_3 asymmetric C–H stretch, by intracavity excitation using the Kiton-Red S-argon-ion laser combination. In one trial, C_2H_2 was excited to (02300) (7390 Å, 38.6 kcal/mole)[20] with the Oxazine-1 perchlorate-krypton-ion laser apparatus (ν_2 is the C≡C stretch). Intracavity power was 5–10 W near 7400 Å and 20–40 W near 6400 Å. Note that for each reaction listed in Table I, the vibrational energy supplied to the reactant exceeds the activation energy for the thermal reaction. Also, the expected temperature rise in the irradiated region is insignificant. For example, based upon the above absorption coefficients and excitation power levels, the rise is calculated to be $\lesssim 1$ °C for the HCl ($v = 6$) + olefin case.[21]

The dye laser was tuned to these weak overtone resonances by optoacoustic detection using the intracavity

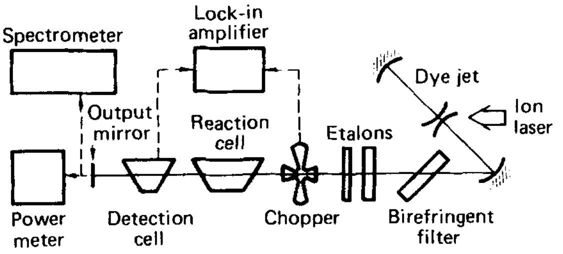

FIG. 1. Experimental layout for intracavity excitation of addition reactions. Reactants are in the reaction cell. The CW dye laser is tuned on resonance by optoacoustic detection with the detection cell. Laser power and wavelength are monitored by an external power meter and spectrometer, respectively.

detection cell having Brewster windows, and which contained a microphone and about 25 torr of the molecule to be vibrationally excited. This miniature microphone (Knowles, Inc.) was biased by 1.3 V and had an internal amplifier. The laser frequency was checked before and several times during each run by temporarily turning on a mechanical chopper (~200 Hz), placed in the dye laser cavity, and measuring the spectrophone signal (1–100 μV) with lock-in detection. Under the conditions of this experiment, the intracavity power did not decrease when the laser was tuned to resonance with the reaction and detection cells in place. Using the spectrophone, the (00500) ← (00000) and (02300) ← (00000) transitions in C_2H_2 were found to be as strong as the HCl $v = 5 \leftarrow 0$ transition.

The Pyrex reaction cells had an i.d. of 1.3 cm and ranged in length from 30–58 cm. As was the case for the detection cell, $\lambda/10$ flat quartz Brewster windows were epoxied to the reaction cell. Grease-free Teflon-FETFE O-ring stopcocks were used to seal off the cell. A port composed of stainless steel tubing and a rubber septum allowed gas chromatographic analysis of products by syringe extraction; to inhibit heterogeneous reactions, in some cells the port was isolated from the reactant cell body by a stopcock. In one cell, wall reactions were inhibited by internally coating the cell with Teflon-S (Dupont), followed by baking the cell. Typical reaction cell pressures were 10–40 torr, with equal partial pressure of each reactant. The cell was first filled with one reactant at its desired partial pressure and was then opened to a large reservoir of the second reactant at the desired total operating pressure for about one second to allow pressure equalization but to prevent back diffusion of the first reagent. This method was employed since reaction mixture preparation involving condensing one reactant in the presence of the other produced addition reaction products, and was therefore unsatisfactory.

The reactants employed in this study were the highest purity obtainable from commercial suppliers. They were used without further purification, with the exception of HBr and HCl. These were stored in glass vessels at 77 °K, and were drawn off as these units were allowed to warm. In the case of HBr, the introduction of any Br_2 impurity was minimized in this manner.

Typical irradiation periods lasted 1–2 h. In the $HCl^{\dagger}$ studies the laser was tuned to the strongest absorption line, $H^{35}Cl$ R(2), while for the C_2H_2 (00500) studies at times the different strong R(J) ($J = 3, 5, 7, 9, 11$) lines were employed. The products were analyzed by gas chromatography with flame ionization detection with a 10%, UCW 982 on Chromosorb W-AWDMCS (20 in. long, 1/8 in. i.d.) column for Reactions 1–4 in Table I, and a Chromosorb 102 (18 in. long, 1/8 in. i.d.) column for Reactions 5–6 in Table I. Retention times of the expected products were determined using commercially obtained samples. Product yields, expressed throughout this report as the ratio of product concentration to that of the hydrocarbon reactant, were compared to those of null runs, for which the experimental procedure was identical to that of laser runs except the sample remained unirradiated during the "irradiation cycle." A null run was performed either immediately before or after each laser run. The sensitivity of detection was sufficient that a product yield of 0.01% could easily be determined.

The $HBr + C_2H_2(00500)$ reaction was attempted both at room temperature and at elevated temperatures. In the latter instance, the 58 cm long reaction cell was placed in a 48 cm long oven, with an open-ended cylindrical hot zone, which was heated to 300 °C. About half the cell was thus maintained to the desired temperature ± 10 °C.

III. EXPERIMENTAL RESULTS

A. Vibrationally excited HCl reactions

The experimental observations are summarized in Table II. No C_2HCl_5 product was observed for the HCl–tetrachloroethylene reaction for either null runs or laser-irradiation runs with HCl excited to either $v = 5$ or 6. After seasoning, the background null run yields for HCl + 1, 3-butadiene were ~0.06 ± 0.03% for both 3-chloro-1-butene and 4-chloro-2-butene, the expected products arising from the Markovnikov 4-centered and the 6-centered transition states, respectively. Essentially, the same yields were also obtained with HCl $v = 5$ or 6 excitation. Reactions 3 and 4 of Table I were performed in the Teflon-coated cell. The only product ever observed in the HCl + 2-methyl-1, 3-butadiene reaction was 1-chloro-3-methyl-2-butene; within the scatter of the data essentially equal yields, 0.13 ± 0.04%, were observed for two null and two laser, HCl ($v = 6$) runs. Similarly, for HCl ($v = 6$) + 1, 3-cyclohexadiene only one product, 3-chlorocyclohexene, was detected; in both laser and null runs the yield was ~ 0.12 ± 0.04%. In summary, no systematic difference in product formation for laser-on and background trials was noticed in any $HCl^{\dagger}$ + olefin reaction. Furthermore, no substances other than the expected addition products were ever observed.

B. Vibrationally excited C_2H_2 reactions

At room temperature, there was no measurable background vinyl bromide formation for the $HBr + C_2H_2$ reaction. In the first laser-induced reaction attempt with 6400 Å incident [$C_2H_2(00500)$ excitation, $p_{HCl} = p_{C_2H_2} = 10$ torr, laser duration = 1 h] the C_2H_3Br yield was 0.4%; however, the yield of this product was found to fluctuate greatly in subsequent experiments. For instance, in one experiment, the yield was only 0.04%. The underlying cause of this erratic behavior was investigated by performing "null" runs during which the reaction cell was placed in the dye laser which was tuned off any C_2H_2 resonance. The amounts of product formed following these procedures were at times also unexpectedly large, ~0.8%. Prior to subsequent runs the HBr storage vessel was meticulously cleaned to remove traces of Br_2. Following this procedure to reduce possible Br_2 impurities, the C_2H_3Br product yield was much smaller, 0.01%, for each $1\frac{1}{2}$-h long irradiation run with the laser tuned either on- or off resonance. One attempt was made to accelerate the $HBr–C_2H_2$ addition reaction with

TABLE II. Results of laser-assisted audition reaction experiments.

Reactants	Product	Pressure[a]	Temp.[b]	Duration[c]	Run[d]	Yield(%)[e]	Additional comments
HCl(v = 5) +							
C_2Cl_4	C_2HCl_5	12	···	2 1/2	N	0.00	
				2	L	0.00	
1, 3-butadiene	3-chloro-1-butene	25	···	2	N	0.03; ~0.02	
				2	L	0.025; 0.02; ~0.02	
	4-chloro-2-butene				N	0.025; ~0.02	
					L	0.08; 0.02; ~0.02	
HCl(v = 6) +							
C_2Cl_4	C_2HCl_5	12	···	2	N	0.00	
				2 1/4	L	0.00; 0.00	
1, 3-butadiene	3-chloro-1-butene	24	···	1	N	0.06	
				2	L	0.045	
	4-chloro-2-butene			1	N	0.08	
				2	L	0.07	
2-methyl-1, 3-butadiene	1-chloro-3-methyl-2-butene	21	···	2	N	0.17; 0.07	Teflon-coated cell
				1; 2	L	0.17; 0.14	Teflon-coated cell
1, 3-cyclohexadiene	3-chlorocyclohexene	21	···	1 1/4; 2 1/3	N	0.06; 0.15	Teflon-coated cell
				2	L	0.12	Teflon-coated cell
C_2H_2(02300) +							
HBr	C_2H_3Br	40	···	1 1/2	N	<0.01	
				1 1/2	L	<0.01	
C_2H_2(00500) +							
HBr	C_2H_3Br	40	···	3	N	0.00	
				1; 2; 1 1/2	L(on)	0.42; 0.16; 0.04	
				1 1/2	L(off)	0.84	
		23	···	1 1/2	N	0.00	Cleansed HBr storage vessel
				1; 1; 1 1/2	L(on)	0.01; 0.01; 0.01	Cleansed HBr storage vessel
				1 1/2	L(off)	0.01	Cleansed HBr storage vessel
		30	Room	2 1/4	N	0.00	58 cm long reaction cell
			300	2	N	0.02	58 cm long reaction cell
			300	2	L(on)	3.18	58 cm long reaction cell
			300	2	L(off)	10.97	58 cm long reaction cell
		30	250	2	L(on)	0.05	New, cleaned cell
			250	2	L(off)	0.05	New, cleaned cell
			300	1	N	0.03	New, cleaned cell

TABLE II (*Continued*)

Reactants	Product	Pressure[a]	Temp.[b]	Duration[c]	Run[d]	Yield(%)[e]	Additional comments
$C_2H_2(00500)+$							
HBr	C_2H_3Br	30	300	2	L(off)	0.23; 6.20; ~0.01; 0.15	New, cleaned cell
			300	2	L(on)	0.61; 0.18	New, cleaned cell
HCl	C_2H_3Cl	44	···	2 1/2; 1 1/2	N	0.00; <0.01	
				2; 1 1/2	L	0.02; <0.01	

[a] The pressure is the total pressure in torr, with both reactants having approximately equal partial pressures.

[b] The temperature is in °C, ellipsis means ambient temperature.

[c] The run duration is in hours; for laser runs it includes only the irradiation times, not other dead time; for null runs it includes the entire run time.

[d] The two run types are null (N), laser (L), with ON and OFF (resonance) variations.

[e] The yield is the fractional conversion in %. The results of different runs are separated by semicolons. When several run times are listed in succession, the related yields are listed in the identical order. The yields of both products in the HCl + 1, 3-butadiene reactions were measured in the same runs.

7395 Å laser irradiation to populate C_2H_2 (02300); still essentially no C_2H_3Br (< 0.01%) was observed. Finally, in the HCl + C_2H_2(00500) study, the yield of C_2H_3Cl was measured to be ~ 0.01% independent of whether the dye laser was tuned on or off a C_2H_2 resonance.

Further study of HBr + C_2H_2(00500) continued with the dye laser-pumped reaction cell placed in an oven. In a null run with no laser incident and the cell heated to 300 °C for 1 h, only 0.03% C_2H_3Br was produced. At 250 °C with the laser tuned either on- or off resonance the yield was 0.05% after a 2-h irradiation. With the cell heated to 300 °C, the yield of product formation showed large run-to-run fluctuations, typically varying from 0.05%–0.60% in experiments with the laser tuned either on- or off resonance.

In conclusion, there was no apparent systematic difference attributable to vibrationally excited C_2H_2, which would have been indicated by a product yield consistently higher with the laser tuned to a C_2H_2 resonance.

IV. DISCUSSION

There was no apparent laser enhancement of reactivity attributable to molecular addition in any case examined in this study. This is quantitatively related to the expected product yields below, where the sensitivity of this experiment is discussed. The only observed laser-related phenomenon was the $HBr + C_2H_2^{\dagger} \rightarrow C_2H_3Br$ reaction in which significant product was formed only when laser excitation was present; however, the product yield was independent of whether or not the dye laser was tuned to an acetylene resonance. This may be attributed to a photo-induced bromine atom chain reaction. Br_2 has a very dense line absorption spectrum near 6400 Å, superimposed on a weak dissociative continuum, with an average spacing between observed absorption lines equal to the Doppler width.[22] Therefore, the following mechanism can account for the C_2H_3Br formation quite independent of the specific dye laser wavelength employed:

$$Br_2 + h\nu(6400\ \text{Å}) \rightarrow Br_2^{*} \ \text{or}\ 2Br\cdot\ , \qquad (\mathrm{I})$$

$$Br_2^{*} + M \rightarrow 2Br\cdot + M\ , \qquad (\mathrm{II})$$

$$C_2H_2 + Br\cdot \rightarrow H\dot{C}{=}CHBr\ , \qquad (\mathrm{III})$$

$$C_2H_2 + Br_2^{*} \rightarrow H\dot{C}{=}CHBr + Br\cdot\ , \qquad (\mathrm{IV})$$

$$H\dot{C}{=}CHBr + HBr \rightarrow C_2H_3Br + Br\cdot\ . \qquad (\mathrm{V})$$

Reactions (III–V) are all exoergic with net enthalpies, −12, −10, and −16 kcal/mole, respectively.[8] (M represents any molecule present.) The activation energy for Reaction (V) is estimated to be ~2 kcal/mole.[23] This mechanism is similar to the standard bromination methods employing either HBr or Br_2.[24] The decrease in C_2H_3Br yield at room temperature when the HBr storage vessel was routinely cleaned and the observation of product formation at 300 °C with the laser tuned off resonance strongly imply that C_2H_3Br was generated by laser-induced bromination.

The anticipated yield of product in the $X^{\dagger} + Y \rightarrow Z$ addition reactions under study can be calculated as follows: The steady state population of the laser-excited molecule X in the laser-prepared vibrational level is $[X^{\dagger}]$ and is determined by

$$\frac{d[X^{\dagger}]}{dt} = \frac{\alpha I[X]}{\hbar\omega} - \gamma_{Q_X}[X^{\dagger}][X] - (\gamma_{Q_Y} + k_R)[X^{\dagger}][Y] = 0\,, \qquad (1)$$

where α is the absorption coefficient, I is the laser intensity, $\hbar\omega$ is the photon energy, γ_{Q_i} is the rate molecule i collisionally quenches X from the laser-pumped state to a lower, unreactive state, and k_R is the reaction rate constant of the vibrationally stimulated addition reaction. Spontaneous emission and losses due to diffusion are negligible. Using $[X^{\dagger}]$ from Eq. (1) the rate of product formation is

$$\frac{d[Z]}{dt} = k_R[X^\dagger][Y] = \frac{\alpha I}{\hbar\omega} k_R \frac{[X][Y]}{\gamma_{Q_X}[X] + (\gamma_{Q_Y} + k_R)[Y]} . \qquad (2)$$

In the reported experiments, $[X] = [Y]$. If the pumping transition is Doppler broadened, the right-hand side (RHS) is proportional to $[X]$; for a pressure-broadened absorption profile ($p_{total} \gtrsim 50$ torr), the RHS is independent of $[X]$ on resonance since α then varies as $1/[X]$. The yield $P = [Z]/([\text{hydrocarbon reactant}] = [X])$ (equivalent to the fractional conversion as defined in Sec. II) is straightforwardly calculated from Eq. (2) assuming small yields, and $[X] = [Y]$; and also correcting for the fact that the laser interacts with only a small fraction (~2%) of the cell's contents.

The following considerations must be incorporated to permit meaningful estimates of P: (1) The vibrational excitation completely removes the reaction barrier, and the laser-induced and associated thermal reactions have equal steric factors (~0.01–0.001), and therefore k_R can be set equal to the frequency factor listed in Table I. (2) The pumped transition is fully Doppler broadened. (3) The rates of collisional quenching must be deduced from previous studies. Several groups[25] have measured the rate of the V–V transfer $HCl(v=2) + HCl(v=0) \rightarrow 2HCl(v=1)$ to be $1.0 \pm 0.2 \times 10^5$/torr-sec. Assuming resonant dipole–dipole transfer and a harmonic model for HCl, the quenching rate of $HCl(v=6)$ to $HCl(v=5)$ by $HCl(v=0)$ should be $\sim 3 \times 10^5$/torr-sec. This value is used here, though the actual rate may be smaller since the "$6+0 \rightarrow 5+1$" reaction has a larger energy defect than the "$2+0 \rightarrow 1+1$" transfer. Multiquantum V–V transfer in HCl should be negligible. The relaxation of $HCl^\dagger$ by the olefins employed in this study has not been investigated. The only previous related study is that by Zittel and Moore[26] of V–V transfer from $HCl(v=1)$ to CH_4 and CD_4, who measured rates of 8.4 ± 0.6 and $1.1 \pm 0.2 \times 10^4$/torr-sec, respectively. Based on these sparse data, it is not unreasonable to also set the rate of quenching of $HCl(v=6)$ by the olefins equal to 3×10^5/torr-sec. This assumed quenching rate constant for either HCl or olefin collision partners may be considered to be physically plausible (or perhaps optimistic); alternately, in a "worst-case" analysis an extremely large value of quenching may be assumed such as $\gamma_Q = 10^7$/torr-sec, which is equal to the gas kinetic collision frequency. Product estimates based both on the "plausible" and "worst-case" rates of quenching are given below.

For the case of $HCl(v=6)$ + olefin reactions pumped by 20 W within the HCl Doppler profile, with $p_{total} = 20$ torr, and a representative value of $k_R = 10^8$ l/mole-sec ($= 5.5 \times 10^3$/torr-sec) (see Table I) after a 1-h irradiation, $P = 5.3\%$ for $\gamma_Q = 3 \times 10^5$/torr-sec, and 0.16% for $\gamma_Q = 10^7$/torr-sec. As can be seen in Table I, for most cases the actual values of frequency factor A are 2–6 times larger than the assumed value of k_R. Approximately the same values for γ_Q can be employed for $HCl(v=5)$. Since compared to the $HCl(v=6)$ case, I decreases by a factor of ~4 while α increases by this same factor, these computed values of P are also valid estimates for the $HCl(v=5)$ reactions. Furthermore, the assumed values of γ_Q probably at worst bracket the actual quenching rates of $C_2H_2^\dagger$. Since the $C_2H_2(00500)$ or (02300) → (00000) transitions are as strong as $HCl(V=5 \rightarrow 0)$, the above bracketed estimates of P are reasonable for the $HBr + C_2H_2$ (02300) reaction but are most likely somewhat low (by a factor of ~4), for the $C_2H_2(00500)$ reactions. Utilizing these considerations, the experimentally observed yields should have been at least ~0.3% for a $1\frac{1}{2}$-h laser-irradiation run, even with severe excited state quenching. It should be noted that the steady state $HCl(v=6)$ population in the laser-irradiated volume are 1.6×10^{10} and 4.8×10^8/cc for the two extreme cases of collisional relaxation.

Based on the sensitivity of this experiment, the investigated addition reactions are apparently at least 10–1000 times slower than expected if the reaction barriers were totally removed (the actual value depending on the true quenching rate γ_Q). This conclusion rests on the assumption that the steric factors for the thermal and vibrationally stimulated reactions are equal; this assumption may not be valid. Birely and Lyman[27] have addressed the questions of what fraction of the vibrational energy which is deposited in a reaction, E_V, actually contributes to lowering the activation energy by the amount αE_V ($\alpha \leq 1$) and whether the excitation also (or only) affects the pre-exponential factor. At present, these questions remain unanswered.

Perhaps these negative results can be explained by the trajectory calculations of Polanyi and co-workers,[1] which describe the $X + YZ^\dagger \rightarrow XY + Z$ and $AB + CD^\dagger \rightarrow AC + BD$ class of reactions. A general conclusion of these studies is that exoergic reactions tend to have reaction barriers in the entrance channel and that relative translational energy is particularly effective in promoting these "early" barrier reactions, whereas, vibrational excitation is noticeably ineffective.[1] Since all the addition reactions under study are quite exoergic, this generalization may explain the negative results. However, this explanation is probably too simplistic, since the employed reactants are more complex than those studied in Polanyi's work and also because the nature of addition reaction dynamics may be quite different than for atom transfer (abstraction) or metathesis reactions.

A more plausible explanation for the failure of the $HCl^\dagger$ + olefin reactions focuses on the complex nature of the reactants. Though energy is preferentially channeled into the hydrogen halide in HX elimination, the reaction dynamics also specify the disposal of the remaining energy into kinetic energy and the olefin's vibrational modes. Since in this experiment the energy deposited in $HCl^\dagger$ exceeded the thermal activation energy in some cases by 20 kcal/mole (an amount almost equal to the activation energy itself), it is unlikely that the addition reaction could be stimulated by exciting HCl in an even higher mode. It is possible, however, that these reactions could be stimulated, if a critical amount of relative translational energy were provided in addition to preparing $HCl^\dagger$, instead of needing to excite all remaining degrees of freedom. However, Clough *et al.*[28] measured the distribution of vibrational–rotational states of HF formed in the decomposition of chemically activated CH_3CF_3, and concluded that most of the available reaction energy is found in the vibrational levels of both the HF and CH_2CF_2 products, with little appearing in translation (or rotation). This suggests that simultaneous vibrational excitation of both reagents, with no increase in relative kinetic energy may, in fact, be required to accelerate some types of addition reactions.

The negative results of the experiments reported here are in accord with other, apparently less extensive, investigations of $HX^{\dagger}$ + olefin addition reactions. Reddy and Berry[16] tried to observe the $HCl(v=6)$ + isobutene reaction using intracavity dye laser overtone excitation without success. It should be noted that the pre-exponential factor for the thermal analog of this reaction is 200 times smaller than for HCl + butadiene, whereas both reactions have approximately equal activation energy.[14] Therefore, in light of the present results it would be certainly surprising if they had observed a vibrationally enhanced reaction. In a similar study, Bauer[17] has apparently failed to observe the addition of $HF^{\dagger}$ to various olefins (C_2F_4, CH_2CF_2, $HC\equiv C-CH_3$, etc.); it is difficult to make a definitive comparison with this study since the sensitivity and many of the details of his experiment were not given in his report. (The experiment was performed at $T = 25$ °C and 190 °C and the HF was pumped by a pulsed HF laser.)

The failure to observe the HBr or HCl + C_2H_2(00500) addition reactions can be more easily rationalized since the excited mode, the C–H stretch, has no component along the reaction coordinate. It should be noted that no product was also observed in the HBr + C_2H_2(02300) trial in which the C≡C stretch is also excited. It is possible that the reaction could be stimulated by pumping solely the ν_2 (C≡C stretch) or ν_4 (C≡C bend) mode. Such experiments could be performed in C_2HD by multiphoton or successive photon[14] pumping of the ν_2 mode, which is resonant with the normal CO laser[29] or exciting the strong first overtone of the ν_4 mode, which is resonant with the normal CO_2 laser.[30] In direct laser excitation of (00500) the number of molecules prepared by collisional pumping into high ν_2 and ν_4 levels is insignificant when compared to the sensitivity of this experiment.

No apparent increase in reactivity was observed for HBr + C_2H_2(00500) at 300 °C. The main effects of this increase in temperature were an increase in average relative translational energy by ~40% and a much larger increase in the small number of molecules in the tail of the Maxwell–Boltzmann distribution with kinetic energy $\gg kT_{\text{room}}$, as compared to the room temperature case. This experiment is sensitive only to the first effect. Therefore, it may be concluded that if a translational energy barrier is the dominant dynamic constraining factor in the HBr + C_2H_2 (00500) reaction, it has a height $> 2kT_{\text{room}}$.

V. CONCLUSION

No evidence for a laser-assisted addition reaction was observed for either $HCl(v=5,6)$ + olefin or for HBr or HCl + C_2H_2 (00500), within the detection limits of this experiment. The upper limit for the rate constants of these reactions was determined to be 10^{-1}–10^{-3} of the frequency factor of the associated thermal reaction; the exact value depends on the employed rates of collisional quenching of the laser-excited levels. Further study of these reactions, in which the degree of excitation of other reagent vibrational modes and the reactant relative translational energy are varied, may provide additional insight into the chemical dynamics of these addition reactions.

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