Infrared Photochemistry of Halogenated Ethylenes

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Abstract: The infrared laser induced multiphoton reactions of mono-, di-, and trichloro-substituted ethylenes have been investigated. In all cases, the dominant mode of reaction is elimination of HCl. Free rotation around the double bond precedes elimination, leading to observable isomerization in 1,2-dichloroethylene and β-d_1-vinyl chloride. The experimental results can be represented in terms of a kinetic model with rates calculated from RRKM theory, which presupposes unhindered redistribution of vibrational energy within the molecule prior to reaction. Comparison of HCl/DCl elimination ratios between $CHD{=}CHCl$ and $CH_2{=}CDCl$ shows that the preferred mode of elimination is α to the chlorine atom. The pressure dependence of this product ratio is not the same for different CO_2 laser lines; however, this ability to influence the outcome of the reaction by changing the laser line is a consequence of differences in energy deposition between one line and another, and not of any mode-selective process. The preference for α-elimination suggests that the reaction may proceed by formation of vinylidenecarbene, followed by rearrangement to form acetylene.

Since the first published report of the dissociation of SF_6 by infrared multiphoton absorption,[1] chemical reactions induced by high-intensity infrared radiation have captured the imagination of a large number of both chemists and physicists. A principal reason for this interest is the apparently substantial difference between the conditions under which such reactions occur and those of normal thermal-equilibrium conditions. In the latter, molecular internal (vibrational) and external (translation/rotational) degrees of freedom are in mutual equilibrium, or very close to it; while in reactions resulting from multiple infrared photon absorption, the energy required to activate the reactive channel is, at least initially, deposited exclusively in the vibrational modes. There has even been speculation that energy could be preferentially localized in one or a few vibrational modes, thereby leading to chemical transformations which are qualitatively different from those observed under conventional conditions. In the experiments reported in this paper, we have studied a series of mono-, di-, and trichloro-substituted ethylenes in order to shed some light on the extent to which nonequilibrium effects may be reflected in overall chemical behavior.

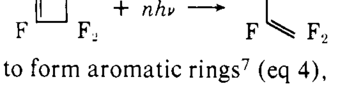
An extensive literature has developed on these reactions in the past 2 years, which is summarized in several reviews.[2] Most of the reactions studied involve homolytic bond cleavage, as in SF_6, SiF_4, NH_3, BCl_3, $CFCl_3$, CF_2Cl_2, and similar systems. More recently, interest has turned increasingly to the types of reactions familiar from conventional thermal chemistry, but carried out under nonequilibrium excitation conditions. Typical examples include elimination of hydrogen halides:[3-5]

$$CH_3CH_2F + nh\nu \rightarrow CH_2{=}CH_2 + HF \qquad (1a)$$

$$(CH_3)_2CHCH_2Br + nh\nu \rightarrow (CH_3)_2C{=}CH_2 + HBr \qquad (1b)$$

$$CH_2{=}CHCl + nh\nu \rightarrow HC{\equiv}CH + HCl \qquad (2)$$

ring-opening reactions[6] (eq 3),



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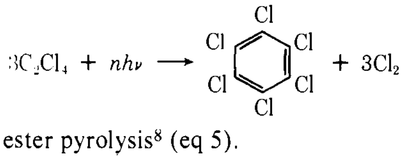
condensation to form aromatic rings[7] (eq 4),



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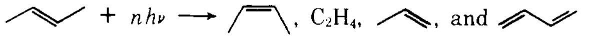
and cyclic ester pyrolysis[8] (eq 5).

$$CH_3COOCH_2CH_3 + nh\nu \rightarrow CH_3COOH + CH_2{=}CH_2 \qquad (5)$$

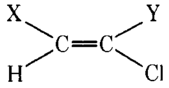
More complex dissociation/isomerization pathways have also been identified as having an origin in specific vibrational excitation,[9] such as eq 6. Reactions 1a and 5, in particular, have



(6)

been shown to be nonthermal in origin[10] by the addition of a "chemical thermometer" to the system, which did not absorb infrared energy directly, but which underwent a reaction when the energy absorbed by a second component of the system was thermalized.[4,8] However, no evidence has been brought forward to date which implies the existence of "mode-specific" reactions, i.e., a chemical transformation resulting from localization of the vibrational energy in some part of the molecule which can be specified by the excitation procedure.[11]

We have carried out a study of reactions induced by multiple infrared photon absorption in a series of chlorine-substituted ethylenes, in order to gain information of use in elucidating the dynamics and detailed mechanisms of this process. The specific systems which have been studied can be represented by the general formula below.



X =	Y =	
H	H	I
H	D	Ia
D	H	Ib
H	Cl	II
Cl	H	III
Cl	Cl	IV

The attractive feature of this series of molecules is that, while the primary laser-induced process is a simple HCl elimination,[5] there are also competitive channels present (such as isomerization or C–Cl bond cleavage) which provide quantitative tests of models for the dynamics of the process. The formation of stable molecular fragments, rather than reactive radicals or atoms, also simplifies the overall kinetics by avoiding secondary reactions. The reactions of the different members of the series provide information on the mechanism and stereochemistry involved, and a sufficient background on conventional thermal reactions of these species exists so that a meaningful comparison may be made between laser- and thermally induced processes. Furthermore, the vibrational spectroscopy of the parent molecules is well characterized, so that quantitative estimates may be made of energy deposition, densities of states, and other parameters required in a detailed theoretical treatment.

Experimental Section

Irradiation System. The infrared source was a Tachisto 215G CO_2 laser furnishing 0.1-1.0 J pulses on lines of the P and R branches of

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the 9.6- and 10.6-μm bands. Each pulse consisted of a 40-50-ns spike containing over 70% of the energy followed by a much lower intensity tail. Transverse mode operation was constrained to TEM_{00} by an intracavity diaphragm. The beam was focused in the reaction mixture by an f.l. = 29 cm AR-coated Ge lens (II-IV Inc.). For some experiments, a collimating telescope was used, consisting of a pair of AR-coated Ge lenses, giving effective apertures between $f/20$ and $f/70$. Reactions were carried out in clean Pyrex cells with NaCl end windows. Care was taken to focus the beam far from either cell walls or windows, in order to avoid the problem of heterogeneous reactions taking place at locally heated surface sites.[12]

Analytical Procedures. Most estimates of the extent of reaction were made by measurement of band intensities of characteristic parent or product molecule infrared absorptions on a Perkin-Elmer 567 spectrophotometer. These measurements were checked against gas-chromatographic analyses on a Carbowax column for the very low-pressure samples. The HCl and DCl bands were *not* used for quantitative analysis, since the intensities of these features are pressure dependent and are not linearly proportional to concentration under our experimental conditions. Measurement of C_2H_2/C_2HD ratios was carried out on a Hitachi RMU-6L GC/MS in the Massachusetts Institute of Technology Mass Spectrometry Facility.

Starting Materials. Vinyl chloride was obtained from a Matheson cylinder, stated purity 99.9%, and transferred to the reaction vessel by a single freeze-pump-thaw cycle.

***α*-*d*₁-Vinyl chloride (Ia)** was synthesized by the method of Francis and Leitch.[13] 1,1,2-Trichloroethane was treated with $Ca(OH_2)$ in an aqueous suspension to yield vinylidene chloride (II). Deuterium bromide was added to this material at −77 °C in the presence of ultraviolet light from photoreactor Hg lamps to produce 1-bromo-2,2-dichloroethane-*2-d*; the composition of the latter product was verified by its NMR spectrum. Addition of the deuterated haloethane to a suspension of zinc dust in boiling ethanol resulted in the evolution of α-d_1-vinyl chloride (Ia). Deuteration at the α position was greater than 96%, based on comparison of the infrared spectrum of the product with published spectra of deuterated vinyl chlorides.[14]

***trans*-*d*₁-Vinyl chloride (Ib)** was prepared by a method similar to that of Nesmeyanov et al.[15,16] A saturated solution of acetylene in 16% aqueous HCl reacted with $HgCl_2$ to form *trans*-2-chlorovinylmercuric chloride (verified by NMR). Treatment of this species with DBr in dioxane (or DBr alone) produced a gaseous product which, after treatment with $AgNO_3$ to remove acetylene, was greater than 96% CHD=CHCl. Infrared spectroscopy showed that the (trans-d_1)/(cis-d_1) ratio was approximately 9:1; this ratio degraded on storage over an extended period of time, or on attempts at further purification.

Vinylidene chloride (II) was either synthesized as described above or purchased from Aldrich Chemical Co. (stated purity, 99%).

***trans*-Dichloroethylene (III)** was obtained from Columbia Organics. No indication of the presence of cis isomer was found in the infrared spectrum.

Trichloroethylene (IV) was Mallinckrodt AR grade.

Results

A. Vinyl Chloride (I). The infrared laser induced chemistry of vinyl chloride was reported in our preliminary communication.[5] The only products observed are HCl and acetylene, indicating a concerted elimination mechanism. The net conversion per laser pulse (CPF) *increases* somewhat over the pressure range 0.5-20 Torr; this is a consequence of increased absorption of infrared energy per molecule in the higher pressure gas. Further details, including optoacoustic measurements of energy deposition, are given elsewhere.[17]

When the infrared beam is focused to a sufficiently small diameter (f.l. of Ge lens $\lesssim$ 5 cm) to cause breakdown to occur in the vinyl chloride sample, additional products are seen. These are principally diacetylene (butadiyne),[18] carbon soot, and a noncondensable gas presumed to be H_2. The formation of such products under focused conditions has been noted by Yogev and co-workers,[9] and most probably involves reactions[19] of ethynyl radicals with the acetylene formed in the elimination step, i.e.

$$\mathrm{C_2H\cdot + C_2H_2 \rightarrow C_4H_2 + H\cdot} \qquad (7a)$$

$$\mathrm{C_2H\cdot + C_4H_2 \rightarrow C_6H_2 + H\cdot} \qquad (7b)$$

etc.

Thermal pyrolysis of vinyl chloride leads to a quite different set of products from that observed following infrared laser photolysis. In a flow system at 500-600 °C, dimerization to chloroprene is observed[20]

$$\mathrm{2CH_2{=}CHCl \rightarrow CH_2{=}C(Cl)CH{=}CH_2 + HCl} \qquad (8)$$

while under static conditions at similar temperature a mixture of products is obtained[21] which includes, in addition to HCl, methane and ethylene in amounts comparable to acetylene, as well as a polymer with $C/H > 1$. Clearly, these results indicate the predominance of free-radical reactions, presumably initiated by C-Cl bond scission, which appear to be absent in the infrared laser induced process. Direct dehydrohalogenation is observed[22] behind shock waves at 1400-2000 K. These experiments[22b] provide a value of the activation energy for the elimination reaction, $E_{act} = (69.3 \pm 2.9)$ kcal/mol.

B. Vinylidene Chloride (II) and Trichloroethylene (IV). Vinylidene chloride and trichloroethylene also undergo elimination of HCl when subjected to intense infrared radiation at ~10 Torr, to form chlorinated acetylenes:

$$\mathrm{CH_2{=}CCl_2} + nh\nu \rightarrow \mathrm{HC{\equiv}CCl + HCl} \qquad (9)$$

$$\mathrm{CHCl{=}CCl_2} + nh\nu \rightarrow \mathrm{ClC{\equiv}CCl + HCl} \qquad (10)$$

Some HC≡CCl is also found in the latter system. Conventional preparations of these chlorinated acetylenes are reported[23] to have low yields, and the resulting products tend to be unstable. By contrast, the mixture containing C_2Cl_2 formed in reaction 10 appears to be stable over an extended period; the C_2Cl_2 did finally explode after repeated transfer, presumably because of leakage of O_2 into the cell.

The C_2HCl observed in the infrared photolysis of IV may have been formed by α,α-elimination or α,β-elimination of Cl_2:

$$\mathrm{CHCl{=}CCl_2} + nh\nu \rightarrow \underset{\llcorner\!\!\rightarrow \mathrm{ClC{\equiv}CH}}{\left[\begin{array}{c}\mathrm{CHCl{=}C{:}}\\ \text{or}\\ \mathrm{\dot{C}H{=}\dot{C}Cl}\end{array}\right]} + \mathrm{Cl_2} \qquad (11)$$

Our experiments cannot distinguish between these two channels for this molecule. The lack of C_2H_2 among the infrared photolysis products of II indicates that α,α-elimination has not occurred for that system. Furthermore, the absence of thermal addition products, such as Cl_3CCH_2Cl, in the reaction mixture indicates that Cl_2 elimination is not a major pathway.

Sudbo et al.[24] report that IV fragments to C_2HCl_2 and Cl atoms in a beam of the parent molecules intersected by CO_2 laser pulses focused with a 25-cm focal length lens. Using similar optics and moderate pressures, we find no evidence for Cl atom production, such as the dimer $C_4H_2Cl_4$ or other recombination products. Using a 5-cm focal length lens and low sample pressures ($\leq$0.1 Torr), Gandini et al.[25] find products resulting from C-Cl cleavage in the infrared photolysis of C_2H_3Cl/C_2H_2DCl mixtures. Again, our experiments do not show products other than those of molecular elimination. Presumably, at high fluences and low pressures used by Gandini or Sudbo, the vibrational energy content of the molecule is driven to much higher levels than in our experiments, where the rate of C-Cl bond scission ($E_0 \sim$ bond enthalpy $\sim$ 90 kcal/mol[26]) may become faster than the lower energy molecular elimination rate (E_0 = 69 kcal/mol).[22b]

We note that the thermal pyrolysis of IV between 385 and 445 °C results in condensation to hexachlorobenzene,[27] a reaction reminiscent of the laser-induced process in tetrachloroethylene-BCl_3 mixtures.

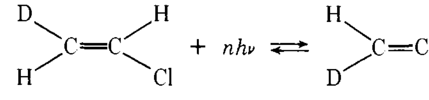
C. *trans*-Dichloroethylene (III). When 5 Torr of III is irradiated with the P(30) [10.6 μm] line of the CO_2 laser, the principal reaction product is *cis*-dichloroethylene. Very little elimination product ($HC{\equiv}CCl$ or HCl) is observed. This result is in agreement with that found by Ambartzumyan et al.,[28a] Nagai and Katayama,[28b] and also Karny and Zare,[12] who report that trans → cis isomerization is the principal laser-induced reaction pathway in this system. This process is also the principal thermal reaction in the system, with an activation energy of 55 kcal/mol;[29] a small amount of condensation to 1,2,4-trichlorobenzene is also reported,[21] which is not found in the laser-irradiated samples.

In interpreting this result, it is important to remember that measurements of product formation are made following a large number (200-2000) of infrared pulses. Initially, both isomerization and dissociation may take place (see following section), but as the irradiation proceeds, an appreciable concentration of *cis*-dichloroethylene accumulates in the cell. This species does *not* absorb CO_2 laser radiation; thus the vibrationally excited trans species is progressively diluted by cold cis molecules. Under the conditions of the experiment, this leads to rapid deactivation of the trans molecules, so that the higher energy HCl elimination channel ($E_{act} \simeq 70$ kcal/mol)[22b] is quenched while the lower energy isomerization channel ($E_{act} = 55$ kcal/mol[29]) is still able to proceed. This point is discussed in more detail in the following section.

D. α-d_1- and *trans*-d_1-Vinyl Chloride (Ia, Ib). In order to investigate the laser-induced elimination reaction in more detail, α-d_1- and *trans*-d_1-vinyl chloride were synthesized as described above and subjected to infrared photolyzing conditions. The resulting reactions were, for the α-d_1 species,

$$CH_2{=}CDCl + nh\nu \nearrow C_2H_2 + DCl \qquad (12a)$$
$$CH_2{=}CDCl + nh\nu \searrow C_2HD + HCl \qquad (12b)$$

while the trans-d_1 initially isomerized (eq 13)



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and subsequently eliminated to form acetylene (eq 14).

$$CHD{=}CHCl + nh\nu \nearrow C_2H_2 + DCl \qquad (14a)$$
$$CHD{=}CHCl + nh\nu \searrow C_2HD + HCl \qquad (14b)$$

The product mixtures from all reactions were carefully examined for evidence of deuterium migration, but none was found; that is, no cis or trans β-d_1 species was formed when starting with the α-d_1, and no α-d_1 was formed when starting with trans-d_1.

A dilution experiment was also carried out on a 1:1 mixture of α-d_1- and h_3-vinyl chloride. The latter component was excited by infrared radiation from the 9.6-μm band of the CO_2 laser, which is not adsorbed by, and has no effect on, the singly deuterated species. The dissociation yield was considerably reduced from that expected from pure vinyl chloride at the same pressure. This is attributed to rapid vibrational deactivation by the unexcited trans-d_1 species present in the mixture; similar behavior was seen in the *trans*-dichloroethylene system, which isomerizes to the nonabsorbing cis form. In a mixture in which *both* species are excited by a given infrared laser frequency, such as the *trans*- and *cis*-d_1-vinyl chloride discussed below, there was no appreciable diminution of the reaction yield.

Branching Ratio for HCl/DCl Elimination. One question we wished to explore was whether there was any preference for elimination from a particular position in the parent molecule, i.e., the branching ratios for reactions 12 and 14. This was investigated by measuring $[C_2HD]/[C_2H_2]$ ratios in the products of these reactions, using GC/MS. In order to make sure that the measured isotope ratios indeed reflected the initial branching ratios, and were not affected by subsequent H-atom exchange, a mixture of C_2D_2 (Merck Sharpe and Dohme; stated deuterium purity >99%) and HCl was analyzed over a 3-day period. This experiment demonstrated two points: (1) The absence of d_2-vinyl chloride in the infrared spectrum of the mixture showed that back-reaction between acetylene and HCl was negligible under our conditions. (2) The infrared spectrum of the acetylene[30] showed that C_2HD made up less than 3% of the total, verifying that H/D exchange also did not occur.

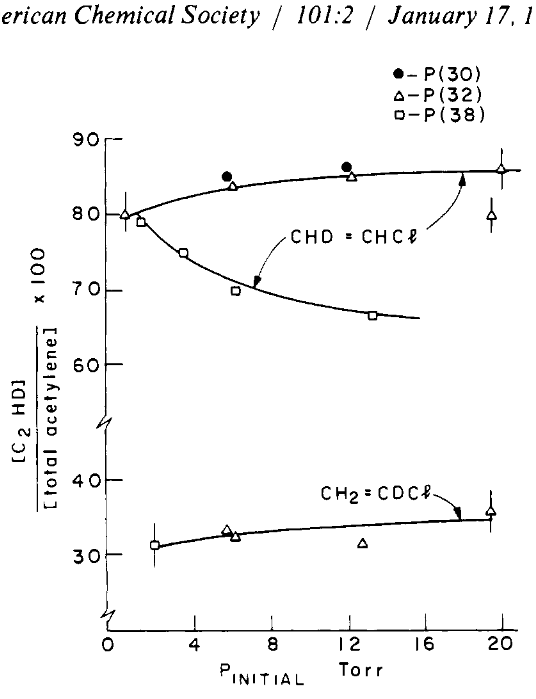

Figure 1. Effective branching ratios for HCl/DCl elimination in infrared laser pumped d_1-vinyl chloride. The CO_2 laser P(30), P(32), and P(38) [10.6 μm] lines were employed, as indicated in the figure. The precision of each determination is ±2%, as shown.

The results of the experiment are shown in Figure 1. As will be discussed shortly, cis-trans isomerization precedes HCl elimination in $CHD{=}CHCl$. Thus, the preponderance of HCl (vs. DCl) elimination in that system could be consistent with either cis, trans, or *gem* elimination. But the opposite result in $CH_2{=}CDCl$, coupled with the lack of H migration across the double bond, can be explained only by strongly favored *gem* or α,α-elimination.

The HCl/DCl elimination branching ratio also displays an interesting dependence on reactant pressure and laser line, shown in Figure 1. For irradiation by the P(32) line, this ratio is nearly constant with pressure (~80% HCl elimination from $CHD{=}CHCl$; ~30% from $CH_2{=}CDCl$). With the P(38) line, however, the HCl elimination ratio from $CHD{=}CHCl$ drops from ~80% to ~65% over the pressure range 1-15 Torr. Several possible explanations for this behavior may be considered.

(1) The elimination of HCl or DCl from a particular site may be specific to the mode excited by the laser, with the mode specificity relaxed by collisions. This is considered particularly unlikely for several reasons. First, the two laser lines [P(32) and P(38)] excite different rotational states of the *same* mode of vibration in the $CHD{=}CHCl$ molecule. Furthermore, all other behavior of this and many other systems is best interpreted in terms of rapid redistribution of vibrational energy within the molecule, rather than by mode-specific excitation.

(2) Some bimolecular process, such as H-atom abstraction,

may tend to make different sites equivalent. Since no radical chain products are found in any of the reaction mixtures, however, this is also considered unlikely. Furthermore, such a mechanism would not be sensitive to which laser line was used to excite the system.

(3) The most probable explanation is in terms of competing unimolecular elimination pathways for α,α- and α,β-elimination, with very similar threshold energies for the two modes of dissociation, as in the case of HX elimination from haloalkanes.[31] Energy deposition studies show that more energy is coupled into the vinyl chloride gas at higher pressures, leading to higher average vibrational excitations.[17] The energy deposition is strongly dependent on which laser line is used. This will be discussed in greater detail in the following section.

Competition between Reaction Pathways. Isomerization vs. Elimination. As noted above, infrared irradiation of *trans*-d_1-vinyl chloride always produced substantial quantities of the cis isomer along with dissociation products. In order to gain information about the competition between the isomerization pathway (reaction 13) and the elimination (reaction 14), a series of experiments was carried out at varying energy fluences through the sample. This was done by condensing the CO_2 laser beam with the two-Ge-lens telescope, which had an *f*/number variable between *f*/20 and *f*/70. A simple treatment of the geometrical optics of the lens system[32] gives, as a first approximation to the peak intensity at the focal point of the beam,

$$I_{\text{peak}} = \frac{P\pi}{f^2\lambda^2} \tag{15}$$

where P is the peak power of the laser pulse (6.7×10^6 W) and λ the wavelength (10.8 μm). Thus the intensity at the focal point varied between 3.3×10^9 W/cm^2 (at *f*/70) and 4×10^{10} W/cm^2 (at *f*/20).

The results are shown in Figure 2. At large *f*/numbers (weak focusing), no HCl or acetylene is produced, and the [cis-d_1]/[trans-d_1] ratio remains at its initial value. As the focusing is increased, isomerization is seen to take place while relatively little dissociation occurs. At the lowest *f*/number optics used, the isomerization appears to level off at a [cis]/[trans] ratio of about 1.2, while extensive dissociation occurs. The equilibrium ratio of the two isomers, calculated as the ratio of vibrational partition functions, was computed to be 0.92 at 300 K and 0.95 for temperatures exceeding 600 K. The somewhat larger experimental value may reflect preferential absorption of the infrared radiation by the trans isomer relative to the cis, leading to a greater degree of dissociation.

The basis of this behavior is the lower activation energy for isomerization relative to HCl elimination.[33] This leads to the possibility of the former reaction taking place at lower vibrational energy content in the vinyl chloride molecule than is required for dissociation.

Comparison with RRKM Theory. A. Kinetic Model. Most detailed treatments of multiphoton induced reactions[35,36] have relied on the solution of a master equation incorporating excitation, relaxation, and reaction terms. From these studies we observe several dynamic features of the population distribution over energy, $f(E)$: (a) The average energy $\langle E \rangle$ of the distribution increases only during the laser pulse. (b) A maximum $\langle E \rangle$ is reached during the pulse where up-pumping is balanced by population loss via reaction of hot molecules. (c) Very little reaction occurs after the pulse because molecules unreacted by the end of the pulse are collisionally deactivated. (d) The shape of the population distribution is nearly identical with a Poisson for $\langle E \rangle$ below the critical energy of reaction. To avoid the lengthy computation and the numerical approximations used to obtain the individual rate coefficients coupling the various energy levels, we have used these observations as the basis of a simplified kinetic model.

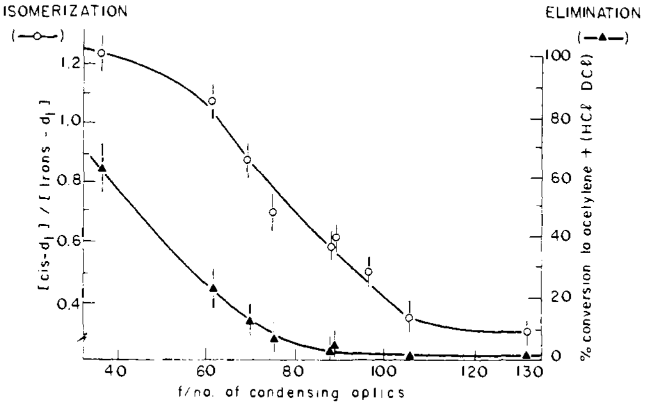

Figure 2. Competition between infrared laser induced isomerization and HCl/DCl elimination in *trans*-d_1-vinyl chloride. All experiments at an initial pressure of 3.2 Torr; 1500 pulses at 10.8 μm with 0.3 J incident energy. The *f*/number is equal to the focal length of the lens combination divided by the diameter of the Gaussian beam.

Our model is based on several assertions. (a) The population distributions are characterized by the average vibrational excitation $\langle E \rangle$ and can be expressed analytically for $\langle E \rangle$ above a few kilocalories per mole. The form of the distribution may be as narrow as a Poisson,

$$f(n) = \frac{e^{-\langle n \rangle} (\langle n \rangle)^n}{n!} \tag{16}$$

with $E = n\hbar\omega$ and $\langle E \rangle = \langle n \rangle \hbar\omega$. Although the master equation treatments predict a Poisson, this may be an artifact of using a harmonic energy grid, thus producing the same distribution as for coherently pumped harmonic oscillators.[37] The broadest distribution possible is the maximal entropy or Boltzmann-like distribution[38]

$$f(E) = \frac{N(E)\, e^{-\gamma E}}{Q} \tag{17}$$

where $N(E)$ is the Whitten-Rabinovitch expression for the density of states,[39]

$$Q = \int_0^\infty N(E) e^{-\gamma E}\, dE \tag{18}$$

and γ is a temperature-like parameter determined from

$$\langle E \rangle = \frac{\int_0^\infty E N(E) e^{-\gamma E}\, dE}{Q} \tag{19}$$

(b) When reaction occurs, the form of the distribution is not greatly affected. For the 3.2 Torr α-d_1-vinyl chloride system used in this model, very little reaction occurs for each pulse. Only the highest energy molecules, comprising a small fraction of the total distribution, react.

(c) In the 1-s interval between laser shots, the products from the reaction zone mix, by diffusion, into the rest of the unreacted cell volume.

(d) Using assertions (a)-(c), the net reaction can be approximated by a continuous process analogous to placing all the brief intervals of reaction back to back. The total time of reaction is then the total number of laser pulses times the reaction time per pulse. This time was chosen as 10^{-7} s/pulse, to include the full laser pulse and to allow for two or three collisions (at 3.2 Torr) during each pulse.

(e) Since the $\langle E \rangle$ of the population distribution is static (observation (b)) during this interval, a constant reaction rate for a particular reaction j can be calculated using RRKM unimolecular reaction rates[40] averaged over the proper population distribution:

Table I. Vibrational Frequencies of Deuterated Vinyl Chlorides and Transition-State Configurations (cm^{-1})

	trans-d_1-vinyl chloride				*cis*-d_1-vinyl chloride			
mode[a]	molecule	isom t.s.	β-elim t.s.	α-elim t.s.	molecule	isom t.s.	β-elim t.s.	α-elim t.s.
(a′) 1	3114	3000	3000	2200	3090	3000	2200	2200
2	3066	3000	2500	3000	3047	3000	3000	3000
3	2231	2200	2200	2030	2210	2200	2500	2200
4	1608	1300	1800	1800	1580	1300	1800	1800
5	1308	1300	1308	1300	1315	1300	1315	1300
6	1237	1237	1240	1130	1328	1328	1320	1250
7	909	700	750	r.c.	909	700	750	r.c.
8	678	650	r.c.	490	710	680	r.c.	490
9	385	350	280	280	368	350	280	280
(a″) 10	947	r.c.[b]	1500	1500	927	r.c.	1500	1500
11	798	700	800	750	790	720	800	750
12	515	515	515	515	543	543	540	540

[a] Number of normal modes in accordance with standard assignment; see ref 29a and 38. [b] r.c. = reaction coordinate.

$$k_j = \int_{E_0}^{\infty} k_j^{\mathrm{RRKM}}(E) f(E)\,\mathrm{d}E \qquad (20)$$

The energy-dependent rates $k_j^{RRKM}(E)$, incorporating the Whitten–Rabinovitch density of states function, are given by

$$k^{\mathrm{RRKM}}(E) = h^{-1}\frac{\sigma_r^{\dagger}}{\sigma_r}\frac{(E - E_0 + a^{\dagger}E_z^{\dagger})^{s-1}}{(E + aE_z)^{s-1}} \times \frac{\prod_{i=1}^{s}\omega_i}{\prod_{i=1}^{s-1}\omega_i^{\dagger}}\,\frac{1 - \beta^{\dagger}\dfrac{\mathrm{d}W^{\dagger}(E'^{\dagger})}{\mathrm{d}E'^{\dagger}}}{1 - \beta\dfrac{\mathrm{d}W(E')}{\mathrm{d}E'}} \qquad (21)$$

with

$$a = 1 - \beta W(\mathrm{E}')$$

$$\beta = \frac{s-1}{s}\frac{\langle\omega^2\rangle}{\langle\omega\rangle^2}$$

$$W(E') = \exp[-2.4191(E')^{0.25}]$$

and $E' = E/E_z$. The ω's are the normal-mode vibrational frequencies, and E_z is the zero-point vibrational energy, for the parent molecule or the transition state (denoted by †). There are $s = 12$ normal modes for the vinyl chloride molecule, and the rotational symmetry numbers $\sigma_r = \sigma_r^{\dagger} = 1$. The vibrational frequencies for the parent *cis*- and *trans*-d_1-vinyl chloride were taken from published analyses of the infrared spectrum,[41] and those for the transition states estimated by standard methods.[42] These frequencies are listed in Table I.

Using these assertions, we can approximate the reaction kinetics of the α-d_1-vinyl chloride system as a set of parallel first-order reactions:

$$(\text{trans-}d_1) \xrightarrow{k_1} (\text{cis-}d_1) \qquad (22a)$$

$$(\text{trans-}d_2) \xrightarrow{k_2} C_2H_2 + DCl \qquad (22b)$$

$$(\text{trans-}d_1) \xrightarrow{k_3} C_2HD + HCl \qquad (22c)$$

and

$$(\text{cis-}d_1) \xrightarrow{k_4} (\text{trans-}d_1) \qquad (23a)$$

$$(\text{cis-}d_1) \xrightarrow{k_5} C_2H_2 + DCl \qquad (23b)$$

$$(\text{cis-}d_1) \xrightarrow{k_6} C_2HD + HCl \qquad (23c)$$

where the k_j are determined only by $\langle E\rangle$ and the choice of distribution in eq 20. In this system, k_1 and k_4 are the rates for cis ↔ trans isomerization. The trans-elimination rate from the trans isomer is k_2; this is set equal to zero, since it is equivalent to isomerization followed by cis elimination. Both β(cis) and α(*gem*) elimination can contribute to k_3. Similarly, k_5 is the rate for β(cis) elimination from the cis isomer, and k_6 is the rate for (*gem*) elimination. Equations 22 and 23 lead, in turn, to a set of coupled equations for the concentrations of *cis*- and *trans*-d_1-vinyl chloride:

$$\frac{\mathrm{d}}{\mathrm{d}t}[\text{trans-}d_1] = -(k_1 + \mathrm{k}_2 + k_3)f[\text{trans-}d_1] + k_4 f[\text{cis-}d_1] \qquad (24a)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\text{cis-}d_1] = k_1 f[\text{trans-}d_1] - (k_4 + k_5 + k_6)f[\text{cis-}d_1] \qquad (24b)$$

The factor f is the fraction of molecules in the cell which are pumped to high vibrational excitation by the focused laser beam. We estimate f to be $\sim 5 \times 10^{-5}$, which is the approximate volume encompassing the reacting molecules[5] divided by the total cell volume ($214\ \mathrm{cm}^3$). Variations of f by ±50% affected the calculated results by only 1–2%.

We find the eigenvalues of eq 24, from the usual determinantal procedure, as

$$r^{\pm} = \frac{1}{2}\{-f(p + q) \pm f[(q - p)^2 + 4k_4k_1]^{1/2}\} \qquad (25)$$

with

$$q = k_1 + k_2 + k_3 \qquad (26a)$$

and

$$p = k_4 + k_5 + k_6 \qquad (26b)$$

The concentrations after an irradiation time t are given by

$$\begin{pmatrix}[\text{trans-}d_1]\\ [\text{cis-}d_1]\end{pmatrix}_t = c_1\begin{pmatrix}1\\ \gamma^+\end{pmatrix}e^{r^+t} + c_2\begin{pmatrix}l\\ \gamma^-\end{pmatrix}e^{r^-t} \qquad (27)$$

In eq 23

$$\gamma^{\pm} = \frac{r^{\pm} + qf}{k_4f} = \frac{k_1f}{pf + r^{\pm}} \qquad (28)$$

The total reaction time was 1.5×10^{-4} s, as mentioned above.

The coefficients c_1 and c_2 are found from the initial conditions, $[\text{trans-}d_1]_{t=0} = c_1 + c_2 = 0.78$ for the sample we used, and

$$[\text{cis-}d_1]_{t=0} = c_1\gamma^+ + c_2\gamma^- = 0.22 \qquad (29)$$

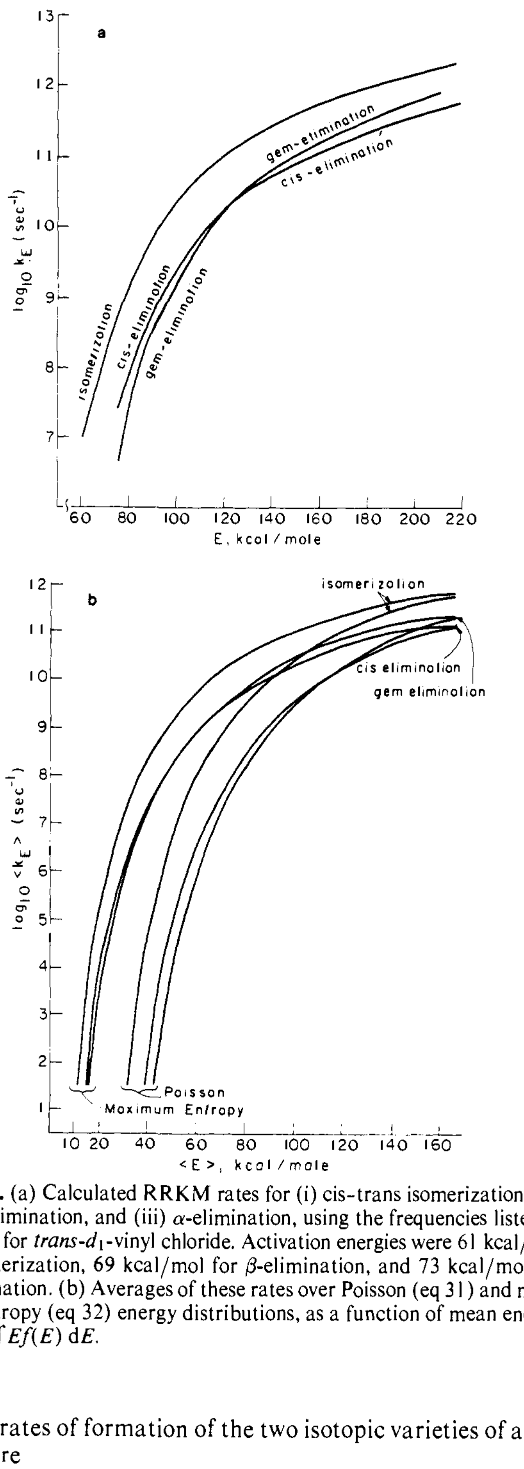

Figure 3. (a) Calculated RRKM rates for (i) cis-trans isomerization, (ii) β(cis)-elimination, and (iii) α-elimination, using the frequencies listed in Table II for *trans*-d_1-vinyl chloride. Activation energies were 61 kcal/mol for isomerization, 69 kcal/mol for β-elimination, and 73 kcal/mol for α-elimination. (b) Averages of these rates over Poisson (eq 31) and maximal-entropy (eq 32) energy distributions, as a function of mean energy $\langle E\rangle = \int Ef(E)\,dE$.

The rates of formation of the two isotopic varieties of acetylene are

$$\frac{d}{dt}[C_2H_2] = fk_2[\text{trans-}d_1] + fk_5[\text{cis-}d_1] \qquad (30a)$$

$$\frac{d}{dt}[C_2HD] = fk_3[\text{trans-}d_1] + fk_6[\text{cis-}d_1] \qquad (30b)$$

Inserting the precursor concentration (27) in eq 30 leads to the solutions

$$[C_2H_2]_t = w(e^{r^+t} - 1) + x(e^{r^-t} - 1) \qquad (31a)$$

and

$$[C_2HD]_t = y(e^{r^+t} - 1) + z(e^{r^-t} - 1) \qquad (31b)$$

with

$$w = \frac{c_1 f}{r^+}(k_2 + k_5\gamma^+) \qquad (32a)$$

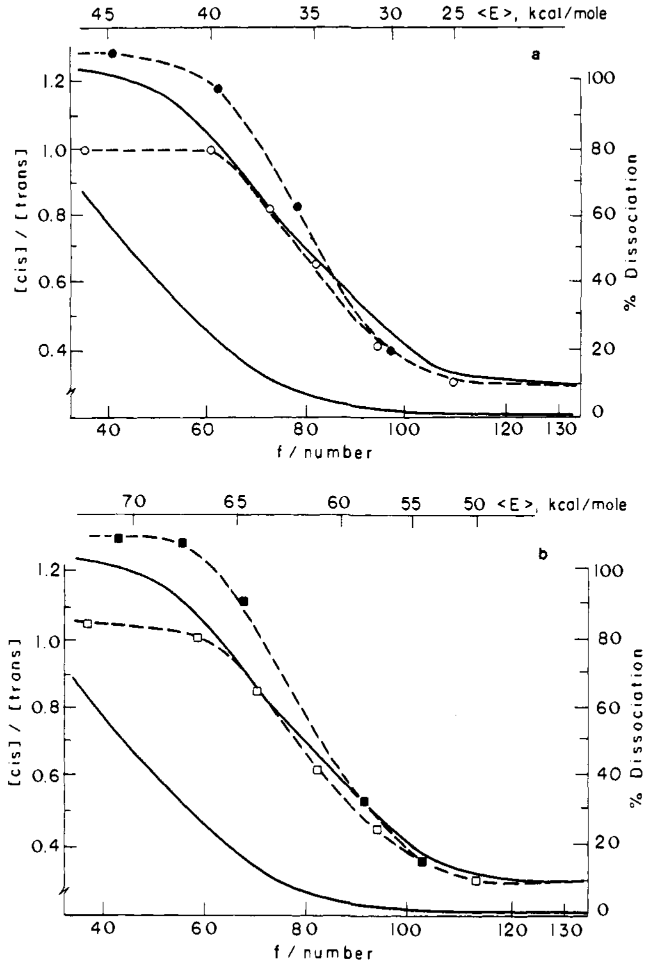

Figure 4. Dissociation (right-hand scale) and isomerization (left-hand scale) yields as a function of f/number and mean energy. The solid curves are experimental data, taken from Figure 2. The dashed curves are the results of the calculations described in this section. Open symbols, $\langle E\rangle_{\text{trans}} = \langle E\rangle_{\text{cis}}$; solid symbols, $\langle E\rangle_{\text{trans}} = \langle E\rangle_{\text{cis}} + 1$ kcal/mol. (a) Calculation with Poisson distribution, eq 31. The values of E_0 are 63, 70, and 69 kcal/mol for isomerization, cis elimination, and *gem* elimination, respectively. (b) Calculation with Boltzmann-like maximal-entropy distribution, eq 32. The corresponding values of E_0 are 61, 69, and 73 kcal/mol.

$$x = \frac{c_2 f}{r^-}(k_2 + k_5\gamma^-) \qquad (32b)$$

$$y = \frac{c_1 f}{r^+}(k_3 + k_6\gamma^+) \qquad (32c)$$

and

$$z = \frac{c_2 f}{r^-}(k_3 + k_6\gamma^-) \qquad (32d)$$

B. Competition between Isomerization and Dissociation. Figure 3 shows a set of calculated RRKM rates for the isomerization, α,α-elimination and α,β-elimination channels, along with averaged rates using both Poisson and maximal entropy distribution functions. For a given mean excitation level $\langle E\rangle$, the value of the averaged rate constant for the Poisson distribution can be many orders of magnitude lower than for the Boltzmann-like distribution. This is a consequence of the more extended "tail" of the latter distribution which, even for low values of $\langle E\rangle$, extends to energies where the k^{RRKM} become large (see ref 38). As noted by Grant et al.,[36] appreciable reaction occurs with a narrow Poisson distribution only at $\langle E\rangle$ close to the E_0 of reaction.

In Figure 4 we show the comparison of relative isomerization/dissociation yields, calculated from the kinetic model and the RRKM rate theory described in the preceding section, with the experimental data. For each limiting form of the vibrational energy distributions, and at several values of incident energy flux Φ (determined from the focal length of the beam condensing optics by eq 15), we found a value of $\langle E \rangle$ which gave the proper percent dissociation of the vinyl chloride into acetylene and HCl. This value was then used to calculate the expected [cis]/[trans] ratio at that energy flux.

As can be seen from Figure 4, either form of the distribution is capable of reproducing the observed yields. The difference is that at any given flux Φ, the value of $\langle E \rangle$ which is required is about twice as high for the narrower Poisson distribution (eq 16) than for the maximal-entropy, or Boltzmann-like, distribution (eq 17). This is just what would be expected from the behavior of the energy-averaged RRKM rates shown in Figure 3b. We also tested the effect of small variations in the activation energies, E_0, for the isomerization and two dissociation channels, within the stated experimental uncertainties for these quantities (± 1–2 kcal/mol); the values listed for the curves in Figures 3 and 4 gave the best agreement with the data. The effect of allowing a small amount of differential excitation between cis and trans molecules is also shown in Figure 4; increasing $\langle E \rangle_{\text{trans}} - \langle E \rangle_{\text{cis}}$ from zero to only 1 kcal/mol causes the limiting [cis]/[trans] ratio at high energy fluxes to increase from 1.05 to 1.25. Since the absorption coefficients for the particular laser line employed are certainly different for the two isomers, such a small amount of differential excitation is quite reasonable, and satisfactorily accounts for the observed ratio.

The principal conclusion from these results is that a statistical, non-mode-specific model provides an excellent description of the laser-induced chemistry taking place in this system. The internal energy distributions are characterized only by a mean energy $\langle E \rangle$, and RRKM rates, which presuppose a free flow of energy throughout the molecule, are employed. It is not possible, however, to specify a unique form of the distribution function without an independent measurement of the absolute amount of energy deposited by the laser field.

C. Stereochemistry of the Elimination Reaction. The preceding calculation also gives α/β elimination ratios which are in agreement with the experimental results shown in Figure 1, namely, 80–90% C_2HD (HCl elimination) from $CHD{=}CHCl$ and 30–40% C_2HD from $CH_2{=}CDCl$. The former ratio *decreases,* and the latter increases, as the mean excitation $\langle E \rangle$ in the system is raised. This $\langle E \rangle$ dependence could explain the pressure dependence found for the P(38) line; increasing vinyl chloride pressure often has the effect of *increasing* the mean excitation of the molecules, since pressure broadening of the absorption lines helps to overcome local saturation effects.[17] The magnitude of this effect would, of course, vary from one line to another, thus accounting for the different behavior following excitation with the P(32) and the P(38) lines. We have, in this case, the ability to influence the outcome of a reaction by selective excitation with one or another laser line. This is *not* a result of any mode-specific excitation, however; in fact, it is just the opposite, since the result is predicted by a statistical (RRKM) model. The effect of changing laser lines is, instead, a more subtle one of varying the amount of energy deposited in the system, which in turn depends on such factors as saturation, frequency matching, and pressure broadening. Clearly, any relationship between excitation frequency and reaction product distribution, which is taken to be evidence for a mode-specific process, must be carefully evaluated in terms of energy deposition in the system before such evidence can be accepted.

The predominant mode of elimination in these systems is seen to be α,α- or *gem*-elimination. Precedents in the literature for this type of reaction are sparse; a general comment that "elimination reactions of halo-olefins to acetylenes . . . proceed best with the elements to be eliminated are located *trans*"[43] is based on a small number of examples, none involving hydrogen halide elimination. Haloalkanes dehydrohalogenate via α,α and α,β channels,[31] but their stereochemistry need not resemble that of the haloolefins. Lee and co-workers[44] have observed α,α-elimination from CO_2-laser-excited $CF_2{=}CHCl$ in a molecular beam, and find no energy barrier in the exit channel for this reaction.

The large fraction of α,α-elimination found in these systems raises the question of whether products characteristic of the possible carbene intermediate could be isolated. Alkylidene carbenes are known in solution,[45-47] but only the difluoro species has been observed in the gas phase.[48] It is possible, though, that with a parent molecule in which the rearrangement to the acetylene were inhibited, the gas-phase carbene could be produced by laser-induced dehydrohalogenation, and that its products could be isolated.

Strauz and co-workers[48] have shown that the mercury-photosensitized reactions of substituted ethylenes proceed with free rotation about the C–C bond and α-elimination to produce the carbene. Recent observations of intersystem crossing induced by multiple infrared photon absorption,[49] along with the similarity of the mercury-photosensitized and infrared-multiple photon pathways in this case, suggest that, when the energy content of the molecule is of the order of 100 kcal/mol, vibronically induced singlet–triplet mixing may occur. This suggests not only that the vibrational energy is freely redistributed among all available modes, but that even the distinction between electronic and vibrational energy may break down.

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Substituent Effects of the Trifluoromethyl Group on Electrophilic Additions to Alkenes. Solvolysis of the Trifluoromethyl Group. Protonation of Alkenes Less Basic Than Ethylene, ρ^+ Values of Deactivated Styrenes, and Reactivity–Selectivity Effects

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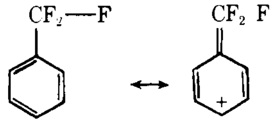
Abstract: Rates of solvent addition to aryl-substituted α-trifluoromethylstyrenes $ArC(CF_3){=}CH_2$ in aqueous sulfuric acid solutions at 25 °C were measured and correlated with the acidity function H_0 of the medium. When aryl is *p*-tolyl the observed reactivity is almost identical with that of ethylene, and for aryl equal to phenyl, *p*-chlorophenyl, and *m*-chlorophenyl the reactivities are distinctly less than that of ethylene. The styrene reactivities are correlated with those of other alkenes by our previously introduced equation $\log k_2 = -10.5\Sigma\sigma_p^+ - 8.92$, and extend the total range of reactivity covered by this equation to 22 orders of magnitude. Ethylene is less reactive than predicted by this equation but is still proposed to react by the same mechanism as the other alkenes, namely, rate-determining protonation on carbon. The low rate is attributed to the inadequacy of the standard σ^+ parameter of hydrogen to fully account for its minimal electron-donating ability in the absence of any other substituent. The reactivity of the styrenes themselves is correlated by the σ_p^+ parameters of the aryl substituents with $\rho^+ = -4.0$. Even in this situation of high electron demand the sensitivity of the reaction to the substituents as measured by the magnitude of ρ^+ is not greatly enhanced. These results show the operation of linear free energy relationships over vast differences in reactivities, with minimal influence of reactivity–selectivity effects.

The trifluoromethyl group is a valuable probe for the study of the interrelation of electronic substituent effects with organic structure, equilibria, and reactivity. Different measurements of the substituent effect of this group are best summarized by the various electronic Hammett σ values: σ_m, 0.42; σ_p, 0.54; σ_m^+, 0.52; σ_p^+, 0.61; σ_I, 0.38; σ_R, 0.18.[1,2] Steric problems with this group are minimized owing to its relatively small size and the absence of any conformational dependence of its substituent effect.

These substituent parameters all emphasize the powerful inductive electron-withdrawing effect of trifluoromethyl. The resonance electron-withdrawing ability of this group as manifested in its σ_R value of 0.18 has been ascribed to the no bond resonance form shown in eq 1.[3] An alternative explanation of this phenomenon is that there is a selective p-π electron donation to the meta position of the benzene ring through resonance interactions as depicted in eq 2.[2] This effect would



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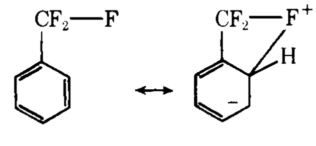

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