together, our final estimates for the ground-state classical barrier and activation energy for the methylcarbyne-vinyl radical isomerization are 8 and 6 kcal/mol, respectively.

Table VI gives the relative energies for the quartet states. On the quartet potential energy surface the energy difference between methylcarbyne and the vinyl radical is very small, the vinyl radical being more stable than methylcarbyne by 2.7 kcal/mol at the highest level of theory applied. The barrier to the quartet isomerization is substantial, 57.0 kcal/mol at the CISD+Q/ANO/ /CISD/TZ+2P level of theory. As for the doublet isomerization, the barrier in the quartet state is lowered considerably when adding polarization functions to the basis set and using correlation methods. The quartet transition state resembles the triplet transition states investigated by Harding³ in having two singly occupied orbitals proximate, and the high barrier to the quartet isomerization can thus be explained by the same argument as used by Harding. In the doublet transition state one of the two orbitals that are singly occupied in the quartet state is unoccupied (the p orbital of a' symmetry on C_1), and, thus, the high spin state is avoided.

Concluding Remarks

From the present study it may be concluded that, at the levels of theory applied, both the ground state and the lowest-lying quartet state of methylcarbyne exist as minima on the respective potential energy surfaces. The classical barrier to the isomerization of the quartet state of methylcarbyne to the corresponding state of the vinyl radical is substantial, 57 kcal/mol at the CISD+-Q/ANO//CISD/TZ+2P level of theory. In contrast, there is a small classical barrier to isomerization on the ground-state potential energy surface, 9 kcal/mol obtained at the CCSD-

(T)/TZ+2P//CISD/TZ+2P level of theory. When the barriers to the isomerization are being predicted, inclusion of polarization functions in the basis set and the effect of electron correlation is important as both lower the barriers considerably. Even though we expect an additional lowering of the barriers when applying higher levels of theory than we have done in this study, we believe that the barriers in both the quartet and ground state will not vanish and will probably be large enough for methylcarbyne to be observable. The final estimate of the ground-state activation energy, obtained by considering the zero-point vibrational energy and correction for the basis set, is 6 kcal/mol.

We have seen that the barrier height for the ground-state isomerization is a bit higher (perhaps 4 kcal/mol⁶) than that for the fleeting, but remarkably well-characterized vinylidene molecule.²⁴ Thus it seems quite plausible that methylcarbyne might also be prepared, identified, and characterized. As one of the most fundamental hydrocarbon fragments, methylcarbyne is clearly an important synthetic target. It may well be that the Colorado group will be able to prepare the anion CH_3C^- and laser photodetach this species to produce methylcarbyne. Such an experiment, of course, might also result in a measurement of the doublet– quartet energy difference.

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Registry No. Methylcarbyne, 67624-57-1; vinyl, 2669-89-8.

(24) See, for example: Ervin, K. M.; Ho, J.; Lineberger, W. C. J. Chem. Phys. 1989, 91, 5974.

Kinetic and Product Distribution Analysis of the Reaction of Atomic Hydrogen with Vinyl Chloride

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An elementary reaction mechanism has been developed to model the experimentally observed loss of vinyl chloride by reaction with atomic hydrogen, as well as the observed products. At the low-pressure, room temperature experimental conditions, the consumption of C_2H_3Cl by reaction with H occurs primarily by nonipso attack by H on the =CH₂ group to form $(CH_3C\cdotHCl)^*$. This energized complex then undergoes an H shift to form $(C\cdotH_2CH_2Cl)^*$, which decomposes to form Cl + $CH_2=CH_2$. Collisional stabilization of the original adduct is also important. Abstraction of Cl by H is negligible at these conditions. Our mechanism is based on quantum Rice-Ramsperger-Kassel (QRRK) analysis of the reactions of the energized adducts from the separately considered ipso and nonipso additions. We also utilized transition-state theory for the isomerization reactions, evaluated with literature rate constants and barriers. We extend the QRRK calculations to higher pressures and temperatures for use by the modeling community. A mechanistic pathway is presented to explain the formation of the various reaction products observed.

Introduction

Displacement reactions involving atomic hydrogen with unsaturated chlorocarbons, specifically chlorinated olefins and aromatics, are considered to be the primary mechanism of dechlorination in high-temperature pyrolysis or incineration of these species.¹ The specific reactions are not elementary, however. They involve the initial formation of a chemically activated adduct by addition of H to the unsaturated bond. This complex can then unimolecularly decompose back to the initial reactants, isomerize (H or Cl shift), decompose to lower energy products, or be collisionally stabilized to a ground state radical adduct. (The overall

(1) Tsang, W. Chemical and Physical Processes in Combustion. Meeting of the Eastern States Section of the Combustion Institute, Orlando, FL, 1990. path to lower energy products might be considered as a displacement.) The reaction to lower energy products often involves production of the corresponding unsaturated hydrocarbon and a Cl atom because the carbon-hydrogen bond formed is stronger than the carbon-chlorine bond broken.

These reactions occur relatively rapidly in the fuel-rich pyrolysis zone of an incinerator or combustor. The importance of these reactions is further amplified because, as will be discussed later, the abstraction reactions $(H + RCl \rightarrow HCl + R)$ have relatively high energies of activation, according to the limited available experimental literature.² Therefore, displacement reaction rates

⁽²⁾ Kerr, J. A., Moss, S. J., Eds. Handbook of Bimolecular and Termolecular Reactions; CRC Press: Boca Raton, FL, 1981; Vol. I, II.

dominate, even at reaction temperatures as high as 1100 K.

The Cl atom product formed in the displacement reaction readily causes a chain in the overall reacting system by rapidly abstracting H from hydrocarbons, forming HCl and hydrocarbon (HC) radicals. Under fuel-rich conditions, these HC radicals often combine, leading to HC molecular weight growth.³

In this study, we focus on a detailed chemical reaction path analysis of H atom reactions with vinyl chloride (C_2H_3Cl). We simulate reported experimental work on this system under conditions of plug flow and pseudo-first-order conditions with C2H3Cl limiting. While the experimental data are not extensive, they do provide calibration for the addition reactions, which must occur initially.

Limited work has appeared in the literature to date on the reactions of H atom with chloroethylenes. Rennert and Wijnen⁴ photolyzed HI in the presence of C₂H₃Cl at 298 K and over a pressure range of 20-130 Torr in a static gas cell. After gas chromatographic analysis of the gas mixture, they concluded that Cl atom abstraction by H was the primary conversion pathway of C₂H₃Cl. Tanner and Jamieson⁵ reacted H atoms, produced by electric discharge, with C_2H_3Cl in a flow system at a pressure of 1.1 Torr, over a temperature range of 300-760 K. Gas chromatographic analyses of the effluent indicated HCl and light HC production from this reaction system.

Jones et al.^{6,7} have offered experimental determinations of the apparent bimolecular rate constants for the reactions of H with various halomethanes and haloethylenes at 298 K and low pressures (<2 Torr). These were obtained in flow tube reactors under pseudo-first-order conditions. Hydrogen atoms were generated in a microwave discharge. Ahmed and Jones⁶ monitored the decay of C_2H_3Cl in excess H, while Jones and Ma⁷ measured H atom decay in excess C_2H_3Cl . Neither of these studies, however, offered any mechanistic description of the conversion of C₂H₃Cl by reaction with H atom.

In this study, we develop a detailed 12-reaction mechanism to describe the $H + C_2H_3Cl$ reaction system. This mechanism is then tested, using the CHEMKIN⁸ integration package with a plug flow reactor configuration, against the experimental pseudofirst-order kinetic data of Ahmed and Jones, and to a lesser extent the product data of Tanner and Jamieson.⁵

Radical addition and recombination reactions were analyzed with energized complex quantum Rice-Ramsperger-Kassel (QRRK) theory.⁹ The high-pressure limit rate parameters required for this technique were obtained from the literature. Where literature data were not available, generic estimates were employed using transition-state theory and thermochemical kinetics, similar to those recommended by Benson¹⁰ or Dean.⁹ Kinetic parameters for the abstraction reactions were obtained from various literature sources. A notable exception is $H + C_2H_3Cl \rightarrow HCl + C_2H_3$, the parameters for which were estimated. This is discussed in detail later.

ORRK Calculations

Energized complex QRRK theory, as presented by Dean,⁹ is used to model reactions where a chemically activated adduct is formed. These involve atom or radical addition to an unsaturated bond and atom + radical or radical + radical recombination reactions. Calculations are based on a geometric mean vibrational frequency (ν) for the adduct. In the current study, the Dean algorithm has been somewhat modified. Gamma function evaluations have replaced factorials for probability and vibrational The Journal of Physical Chemistry, Vol. 96, No. 6, 1992 2495



Figure 1. Potential energy diagram for $H + C_2H_3Cl$ (ipso addition).

TABLE I: $H + C_2H_3Cl = [C_2H_4Cl]^* = Ipso Addition Products^a and$ **Apparent Reaction Rate Constants Predicted Using Bimolecular** QRRK Analysis (Valid for 300-1800 K)

k		A	f i	E _a ª	source
1		1.5E+1	3	5.8	Ь
-1		1.4E+1	3 4	2.1	с
2		3.9E+1	3 2	1.7	d
<υ σ	$\langle v \rangle = 1244/cm$ $\sigma = 4.84 \text{ Å} \epsilon/k = 379.2 \text{ K}$				
bath	Р,		<i>A</i> ,		Ε,
gas	Torr	reaction	cm ³ /(mol·s)	n	kcal/mol
He	1	$H + C_2 H_3 Cl =$ $[CH_2 ClC_2 H_3]^0$	5.43E+20	-4.17	7.77
	760	$H + C_2 H_3 Cl =$ [CH_2ClC+H_3] ⁰	4.62E+23	-4.18	7.82
	1	$H + C_2 H_3 Cl =$	1.60E+13	-0.01	5.81
	760	$H + C_2H_3Cl = C_2H_4 + Cl$	1.82E+13	-0.02	5.86

^aSee Figure 1 for potential energy diagram. Units: A_f, bimolecular, $cm^3/(mol \cdot s)$; E_a , kcal/mol. A_f , unimolecular, 1/s. In all tables $E+x \equiv$ ×10^x. ${}^{b}A_{1} \sim 0.5A_{f}$ for H + C₂H₄ (3E+13, ref 11); E_a from interpolation (see text). Creverse reaction (k_{-1}) from thermodynamics A_{f} , and microreversibility. ${}^{d}E_{a} = \Delta H_{r} + 1.0$; A_{2} for β scission from thermodynamics, A_{-2} for Cl + C₂H₄ (2E+13, ref 2), and microreversibility. Geometric mean vibrational frequency from CPFIT (THERM) program (ref 17) and C_p data. ^fLennard-Jones parameters estimated from properties for C_2H_5Cl (ref 22).

partition function estimation. Barriers $(E_a/h\nu)$ are not rounded to the nearest integer before summations with respect to energy. Summations are therefore not terminated at integer values of energy $(E_i/h\nu)$. This is believed to give better estimates, especially at low temperatures where small changes in barrier height can have a profound effect.

Atomic H + Vinyl Chloride

Addition at the =CHCl Carbon (IPSO). Hydrogen atom can add to either side of the double bond of C₂H₃Cl to form an activated $C_2H_4Cl^*$ complex. Let us consider the attack by H atom ipso to the Cl to form $C \cdot H_2 C H_2 Cl^*$. The energy diagram for this reaction is shown in Figure 1. The reaction products C_2H_4 + Cl are exothermic relative to the energy of the initial reactants and so constitute a low-energy exit channel.

The kinetic parameters input to the QRRK calculation, along with appropriate references, are listed in Table I. We estimate the high-pressure limit A factor for ipso H addition to C_2H_3Cl to be $1.5 \times 10^{13} \text{ cm}^3/(\text{mol}\cdot\text{s})$. This is less than one-half of the comparable value for H atom addition to C_2H_4 given by Allara and Shaw.¹¹ It is similar to higher temperature A factors given for H addition to chlorobenzene (C₆H₅Cl) [1.5 × 10¹³ by Ritter et al.¹² and 2.2 \times 10¹³ by Tsang¹³]. We note that these values

⁽³⁾ Dean, A. M. J. Phys. Chem. 1990, 94, 1432.

⁽⁴⁾ Rennert, A. M.; Wijnen, M. H. J. Ber. Bunsenges Phys. Chem. 1968, 72, 222

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(6) Ahmed, M. G.; Jones, W. E. Can. J. Chem. 1985, 63, 2127.
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^{8003.} Sandia National Laboratories, Albuquerque, NM, 1980

⁽⁹⁾ Dean, A. M.; Ritter, E. R.; Bozzelli, J. W. Combust. Sci. Technol. 1991, 80, 63

⁽¹⁰⁾ Benson, S. W. Thermochemical Kinetics, 2nd ed.; Wiley: New York, 1976.

⁽¹¹⁾ Allara, D. L.; Shaw, R. J. Phys. Chem. Ref. Data 1980, 9, 3, 523.



Figure 2. Pressure dependence of the apparent bimolecular rate constants for $H + C_2H_3Cl$ (ipso addition).



Figure 3. Temperature dependence of the apparent bimolecular rate constants for $H + C_2H_3Cl$ (ipso addition).

for $H + C_6H_5Cl$ can be considered as lower limits for the $H + C_2H_3Cl$ case.

The activation energy E_a used for ipso H addition to C_2H_3Cl was 5.8 kcal/mol. This value is an interpolation between two limits. The upper limit is an E_a of 9.5 kcal/mol for addition of H to C_2Cl_4 and ipso addition of H to C_6H_5Cl , both recommended by Tsang.^{13,14} The lower limit is an E_a of 2.7 kcal/mol for H addition to C_2H_4 , based on experimental data from Allara and Shaw.¹¹ Our value of 5.8 kcal/mol for this ipso addition is also consistent with the ab initio calculations of Schlegel and Sosa,¹⁵ who suggested an E_a of 4–6 kcal/mol.

Figure 2 shows the QRRK-calculated apparent rate constants for the reaction of $H + C_2H_3Cl$ to the stabilization and $C_2H_4 + Cl$ product channels as a function of pressure at 300 K, the experimental temperature of Ahmed and Jones,⁶ and at a typical combustion temperature of 1800 K. In the region of 1 Torr, adduct collisional stabilization is far exceeded by adduct unimolecular decomposition (beta scission) to the low-energy exit channel. At 300 K, stabilization does not become comparable to the $C_2H_4 + Cl$ channel until about 7600 Torr.

(18) Warnatz, J. Rate Coefficients in the C/H/O System. In Combustion Chemistry; Gardiner, Jr., W. C., Ed.; Springer-Verlag: New York, 1984.



Figure 4. Potential energy diagram for $H + C_2H_3Cl$ (nonipso addition).

TABLE II: $H + C_2H_3Cl = [C_2H_4Cl]^* = Nonipso Addition Products^a$ and Apparent Reaction Rate Constants Predicted Using BimolecularQRRK Analysis (Valid for 300–1800 K)

	k	Aª		$E_a{}^a$	sourc	e
	1	2.0	E+13	2.9	b	
	-1	3.5	E+13	43.2	С	
	4	6.4	E+12	38.0	d	
	-4	3.5	E+12	34.0	е	
	5	3.9	E+13	21.7	ſ	
	$\langle v \rangle = \sigma = 4$	1237/cm .84 Å ε/k	k = 379.2 K		g h	
bath	Ρ,		A_{3}		Ε,	
gas	Torr	reaction	cm ³ /(mol·s)	n	kcal/mol	range
He	. 1	$H + C_2H_3Cl =$	4.60E+41	-9.57	11.3	k
	760	$H + C_2 H_3 Cl =$	1.61E+38	-7.62	13.2	j
	1	$H + C_2 H_3 Cl =$	3.20E+24	-5.32	5.97	i
	760	$H + C_2H_3Cl =$	1.38E+31	-6.22	13.6	j
	1	$H + C_2H_3Cl =$	3.16E+16	-1.06	3.92	i
	760	$H + C_2H_3Cl = C_2H_4 + Cl$	1.36E+23	-2.78	12.6	j

^aSee Figure 4 for potential energy diagram. Units: A_f , bimolecular, cm³/(mol·s); unimolecular, 1/s. E_a , kcal/mol. ^b $A_1 \sim 0.5A_f$ for H + C₂H₄ (3E+13, ref 11); E_a from optimization. ^c Reverse reaction (k_{-1}) from thermodynamics, A_1 , and microreversibility. ^d $E_a = 27 + 7 + 4$ (ring strain + abstraction $E_a + \Delta H_r$); $A_4 = 10E+13.2 \times 10E-4/4.6 \times$ 3 (*ekT/h* exp(ΔS_r) × reaction degeneracy) for T = 300 K. ^eReverse reaction (k_{-4}) from thermodynamics, A_4 , and microreversibility. ^f $E_a = \Delta H_r + 1.0$; A_5 for β scission from thermodynamics, A_{-5} for Cl+C₂H₄ (2E+13, ref 2), and microreversibility. ^gGeometric mean vibrational frequency from CPFIT (THERM) (ref 17) and C_p data. ^h Lennard-Jones parameters estimated from properties for C₂H₅Cl (ref 22). ⁱValid from 300 to 1800 K. ^jValid from 600 to 1800 K. ^kValid from 900 to 1800 K.

Temperature dependence of the QRRK results is presented in Figure 3 with rate constants for H atom addition (ipso attack) to C₂H₃Cl at 1 and 760 Torr. (The rate constant for Cl abstraction by H, to be discussed shortly, is also shown for comparison). Adduct stabilization to C·H₂CH₂Cl clearly demonstrates non-Arrhenius behavior. The C₂H₄ + Cl product channel, on the contrary, behaves in an Arrhenius fashion representative of the barrier for H addition, independent of pressure up to 7600 Torr. These results are also presented in equation form (Table I) as a nonlinear, least-squares fit to the form $k = AT^n \exp[-E/(RT)]$.

Addition at the =CH₂ Carbon (Nonipso). The addition of the H atom nonipso to the Cl also occurs, producing an activated CH₃C·HCl^{*} complex. The energy diagram for this addition and the disposition of the adduct is shown in Figure 4. Elimination of the Cl atom via beta scission from the chemically energized complex requires that the radical be on the non-Cl containing

⁽¹²⁾ Ritter, E. R.; Bozzelli, J. W.; Dean, A. M. J. Phys. Chem. 1990, 94, 2493.

⁽¹³⁾ Cui, J. P.; He, Y. Z.; Tsang, W. J. Phys. Chem. 1989, 93, 724.

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 (15) Schlegel, H. B.; Sosa, C. J. Phys. Chem. 1984, 88, 1141.

⁽¹⁶⁾ Westmoreland, P. R.; Howard, J. B.; Longwell, J. P.; Dean, A. M. AIChE J. 1986, 32, 12, 1971.

⁽¹⁷⁾ Ritter, E. R.; Bozzelli, J. W. Int. J. Chem. Kinet. 1991, 23, 767. Ritter, E. R. Ph.D. Thesis, Department of Chemical Engineering, New Jersey Institute of Technology, Newark, NJ, 1989. Ritter, E. R. J. Chem. Inf. Comput. Sci. 1991, 31, 400.



Figure 5. Pressure dependence of the apparent bimolecular rate constants for $H + C_2H_3Cl$ (nonipso addition).



Figure 6. Temperature dependence of the apparent bimolecular rate constants for $H + C_2H_3Cl$ (nonipso addition).

carbon. Therefore, isomerization of the complex must occur via a 1,2 hydrogen shift to allow for the Cl elimination. The barrier for this shift, 38 kcal/mol, is the sum of the ΔH_r (4), ring strain (27), and the barrier for abstraction of H by a carbon radical (7). The isomerization, with subsequent unimolecular dissociation to C_2H_4 + Cl, represents a chemically activated exit pathway with products 15.7 kcal/mol lower in energy than the initial reactants.

The QRRK input parameters for this case are given in Table II. For the nonipso H addition to C_2H_3Cl , the high-pressure A factor chosen is 2.0×10^{13} cm³/(mol·s). This is one-half of the A factor for H + C_2H_4 as recommended by Allara and Shaw.¹¹ The E_a value of 2.9 kcal/mol used in this study was obtained from an optimization in our modeling comparison to the experimental data of Jones et al.^{6,7} This will be discussed in more detail later. While this value is slightly higher than the E_a for H + C_2H_4 (2.7 kcal/mol)-as recommended by Allara and Shaw,¹¹ it is clearly in the range of experimental uncertainty seen in the data review of Jones and Ma.⁷

Ab initio calculations by Schlegel and Sosa¹⁵ suggest an E_a of 1 kcal/mol for this nonipso addition. In order to achieve agreement of our model with the experimental data using $E_a = 1$, the required preexponential factor A_f is 8.4×10^{11} cm³/(mol-s). This value is unrealistically low for such a reaction.

The calculated apparent rate constants for $H + C_2H_3Cl \rightarrow$ nonipso addition products versus pressure at 300 and 1800 K are shown in Figure 5. At 300 K, the isomerization/decomposition route to $C_2H_4 + Cl$ is the primary product channel up to about 10 Torr. Stabilization of the CH₃C-HCl adduct dominates at higher pressures. At 1800 K, however, the $C_2H_4 + Cl$ pathway dominates over stabilization up to about 7600 Torr. Falloff at 1800 K for this channel begins slightly above 760 Torr, whereas, at 300 K, it begins at about 1 Torr.

Figure 6 shows the calculated apparent rate constants for H + C_2H_3Cl (nonipso attack) as a function of temperature at 1 and



Figure 7. Evans-Polanyi plot for Cl abstraction by H atom: (1) H + $Cl_2 = Cl + HCl;$ (2) H + $CCl_4 = HCl + CCl_3;$ (3) H + $CH_2Cl_2 = HCl$ + $CH_2Cl;$ (4) H + $CH_3Cl = HCl + CH_3;$ (5) H + $CF_3Cl = HCl + CF_3;$ (6) H + $C_2H_3Cl = HCl + C_2H_3;$ points 1-5 (ref 2), point 6 (this work).

760 Torr. The abstraction rate constant is also shown for comparison. Regressed results in equation form are shown in Table II. The stabilization channels for either pressure clearly demonstrate non-Arrhenius behavior above about 700 K. At 1 Torr, the isomerization/decomposition pathway to $C_2H_4 + Cl$ dominates over the 300-1800 K range, while at 760 Torr this path requires temperatures greater than 1100 K.

Bimolecular QRRK analyses has shown that the products of the addition reaction $H + C_2H_3Cl$ depend on the temperature and pressure. The elimination of Cl via a low-energy exit channel for the chemically activated adduct was first suggested by Tanner and Jamieson⁵ using a thermochemical argument. However, no quantification was offered as to the pathway or kinetics.

Ahmed and Jones⁶ suggested that C_2H_3Cl conversion occurred via H addition to form an excited $C_2H_4Cl^*$ complex. According to their hypothesis, this complex was then only allowed to decompose back to reactants and/or collisionally stabilize. No decomposition of the chemically activated complex was considered, even though the experiments were performed at low pressures. The stable C_2H_4Cl adduct was then allowed to combine with another H to form an excited C_2H_5Cl , which would then undergo molecular elimination to form C_2H_4 and HCl. Our analysis has indicated a different pathway to products.

Abstraction. Rennert and Wijnen⁴ proposed that H atom abstracts Cl from C₂H₃Cl to form HCl and vinyl radical (C₂H₃). This reaction is exothermic by 10.2 kcal/mol at 298 K, assuming a heat of formation of 69.0 kcal/mol for C₂H₃ (ref 21a) and 5.0 kcal/mol for C₂H₃Cl (ref 10). We estimate the activation energy for this reaction from an Evans-Polanyi plot (Figure 7) of selected reactions where H abstracts Cl. For H abstraction of Cl from C₂H₃Cl, the best fit of the data yields an activation energy (E_a) of 10.4 kcal/mol. We estimate an Arrhenius preexponential factor of 1.0 × 10¹³ cm³/(mol·s), which is similar to A_f values for H abstraction of Cl from saturated chlorocarbons.²

Abstraction of Cl by H is comparable in magnitude to the important addition product channels only above 2500 K. At 300 K, the abstraction channel rate constant is orders of magnitude below our calculated primary addition reaction paths and cannot explain the observed experimental data of Ahmed and Jones.⁶

Evaluation of Mechanism

Pseudo-First-Order Reaction of H + C₂**H**₃**Cl.** Our mechanism, shown in Table III, was evaluated at 298 K and 1 Torr total pressure using CHEMKIN configured for a plug flow reactor. A listing of the species thermodynamics (standard heats of formation and entropies) used in the present simulation is given in the Appendix (Table VII). Pressure dependencies at 298 K, as calculated by energized complex QRRK, were incorporated for radical addition and recombination reaction paths. The initial molar ratio of H/C_2H_3Cl was 100/1. The feed concentrations

TABLE III: Reduced Reaction Set² for $H + C_2H_3Cl$ System Input to

 CHEMKIN

	А,		Ε,	
reactions	cm ³ /(mol s)	n	cal/mol	note
$H + H + M = H_2 + M$	2.5E+17	0	0	ь
He/0.0035/				
$H_2/0.005/$				
$H_2 + CI = HCI + H$	1.2E+13	0	4300	Ь
H + Cl + M = HCl + M	1.4E+18	0	0	Ь
He/0.018/				
$H_2/0.025/$				
$H + C_2H_3Cl = C_2H_4 + Cl$	1.91E+13	0.0	3103	c, d
$H + C_2H_3C = CH_3C \cdot HC$	1.35E+27	-5.12	5310	с
$H + CH_3C + HCl =$	5.46E+15	-0.69	460	с
$C_2H_4 + HCl$				
$H + CH_3 = CH_4$	2.97E+17	-2.41	610	е
$\mathbf{H} + \mathbf{C}_2 \mathbf{H}_4 = \mathbf{C}_2 \mathbf{H}_5$	2.98E+24	-4.23	4430	ſ
$H + C_2H_5 = CH_3 + CH_3$	1.90E+14	-0.01	20	g
$CH_3 + CH_3 = C_2H_6$	1.41E+26	-4.50	2450	8
$Cl + CH_4 = HCl + CH_3$	3.09E+13	0.0	3600	Ь
$Cl + C_2H_6 = HCl + C_2H_5$	7.0E+13	0.0	1000	b

^a Forward rate constants of the form $k_f = AT^n \exp(-E/RT)$; All reactions reversible. Temperature range, 300-800 K. Pressure, 1 Torr. Bath gas; He. ^bReference 2. ^c From QRRK (see separate tables). ^d Rate expression shown is sum of ipso and nonipso cases. ^eReference 18. ^fReference 16. ^gReference 19.

TABLE IV: Conditions for CHEMKIN Simulations



Figure 8. Calculated decay of C_2H_3Cl based on reduced mechanism at 300 K and 1 Torr; Experimental data points of Ahmed and Jones.⁶

used in our simulation are presented in Table IV.

The conversion of C_2H_3Cl was considered after a residence time of 16 ms. Over this period, the model indicated a maximum drop in H atom concentration of 5%, thus supporting the assumption of pseudo-first-order kinetics for the purpose of obtaining an apparent bimolecular rate constant for the H + C_2H_3Cl reaction. These conditions reflect those used in the experiments of Ahmed and Jones.⁶

The apparent rate constant value obtained with the current model analysis is 1.39×10^{11} cm³/(mol·s) at 300 K and 1 Torr (see Figure 8). This value is in excellent agreement with the average apparent experimental bimolecular rate constant, 1.43 $\times 10^{11}$ cm³/(mol·s) listed by Jones and Ma⁷ for H + C₂H₃Cl over the pressure range of 0.55–1.3 Torr, which included the results reported by Ahmed and Jones.⁶

Additional analyses of QRRK results, combined with model integration over this pressure range, suggested a negligible pressure dependency of the apparent bimolecular rate constant for $H + C_2H_3Cl$ over the experimental pressure range. This is also sug-

TABLE V: Relative Importance of H Atom Reactions Which Directly Consume C_2H_3Cl in This System (T = 300 K, P = 1 Torr)

reaction	rate const,	rel
Teaction	cm ² /(mors)	
$H + C_2H_3Cl = C_2H_4 + Cl \text{ (ipso)}$	8.92×10^{8}	negligible
$H + C_2H_3Cl = C \cdot H_2CH_2Cl \text{ (ipso)}$	5.64×10^{4}	negligible
$H + C_2H_3Cl = C_2H_4 + Cl \text{ (nonipso)}$	1.04×10^{11}	0.74
$H + C_2H_3Cl = CH_3C \cdot HCl$ (nonipso)	3.56×10^{10}	0.26
$H + C_2H_3Cl = C \cdot H_2CH_2Cl$ (nonipso)	9.59 × 106	negligible
$H + C_2H_3Cl = C_2H_3 + HCl (abstrn)$	2.65×10^{5}	negligible
н		
м		
	1	
	1	
1 1		
$H \xrightarrow{\qquad} C_2 H_4 + CI \qquad C_2 H_4 + H$	ICI	
м	t	— н
$H \longrightarrow C_1 H_2 \longrightarrow CH_1 + CH_2 + $	сн	
2 5 3	<u> </u>	CH₄
CI	М	·
1	H + CI = HC	X + H
м ↓	2	
$CH_3 + CH_3 \longrightarrow C_2H_6$	H + H + M	\rightarrow H ₂ + M
+	H + CI + M	

Figure 9. Major reaction pathways under conditions: 300 K, 1 Torr, t = 0-16 ms; He diluent, $[H]_0 \gg [C_2H_3Cl]_0$.

gested by the lack of any pressure dependencies in the experimentally observed apparent bimolecular rate constants for H + C_2H_3Br and H + C_2H_3F listed by Jones and Ma.⁷

Table V summarizes the relative importance of H atom reactions which directly consume C_2H_3Cl under the conditions of Ahmed and Jones⁶ (300 K, 1 Torr, $[H]_0 \gg [C_2H_3Cl]_0$). The CHEMKIN analysis indicates that 74% of the calculated apparent rate constant for $H + C_2H_3Cl \rightarrow$ products is due to the addition/chemically activated isomerization/decomposition reaction

$$H + C_2 H_3 Cl \xrightarrow{\text{net}} C_2 H_4 + Cl$$
(1)

The remaining 26% is accounted for by the addition/stabilization reaction.

$$H + C_2 H_3 Cl \xrightarrow{M} CH_3 \dot{C} HCl$$
(2)

The ipso attack channels have negligible contributions to the consumption of C_2H_3Cl by H. At these conditions (300 K, 1 Torr), all of the C_2H_3Cl reaction with H occurs via nonipso addition.

The reason for this phenomenon lies with the activation energy for the addition. As discussed earlier, a value of $E_a = 5.8$ kcal/mol was used for the ipso addition. This value effectively shuts down the ipso attack compared to the nonipso at 300 K. The $E_a = 2.9$ kcal/mol for nonipso addition was optimized to achieve an apparent rate constant for disappearance of C₂H₃Cl in agreement with the Ahmed and Jones⁶ data.

Figures 2 and 5 show that reaction pathway 1 is essentially pressure independent at 300 K in the pressure range of interest (<5 Torr). This further supports the above contention that, at these conditions (300 K, 1 Torr), the observed $H + C_2H_3Cl$ reaction is effectively pressure independent.

Reaction Products. No indication of the major reaction products was given by Jones et al.^{6.7} Tanner and Jamieson⁵ observed CH₄, C_2H_6 , C_2H_4 , and HCl. In addition to accounting for C_2H_3Cl consumption, the present mechanism (Table III) is used to generate concentration/reaction time profiles which reveal how these product species are formed.

In the experiments of Ahmed and Jones,⁶ the initial H/C_2H_3Cl molar ratios were about 100/1. This ensured that the major

TABLE VI: $H + CH_3C \cdot HCl = [C_2H_5Cl]^* = Products^a$ and Apparent Reaction Rate Constants Predicted Using Bimolecular QRRK Analysis (Range 600–1800 K)

	k			E _a ^a		source	
	1	5.0E+13		0.0	Ь		
	-1	1.4E+15		95.7	c		
	2	2.2E+15		84.1	d		
	3	1.3E+17	1.3E+17		е		
	4	6.4E+12		52.8	f		
	$\langle v \rangle = 1301$	/cm			g		
$\sigma = 4.84 \text{ Å}$		$\epsilon/k = 379.2 \text{ K}$	$\epsilon/k = 379.2 \text{ K}$		h		
bath	Р,		A ₃ ,		Ε,		
gas	Torr	reaction	cm ³ /(mol·s)	n	kcal/mol	range, K	
He	1	$\mathbf{H} + \mathbf{C}\mathbf{H}_{3}\mathbf{C}\cdot\mathbf{H}\mathbf{C}\mathbf{I} = [\mathbf{C}_{2}\mathbf{H}_{5}\mathbf{C}\mathbf{I}]^{0}$	3.72E+39	-9.00	8.84	600-1800	
	760	$H + CH_3C \cdot HCI = [C_2H_5CI]^0$	1.69E+43	-9.14	11.7	600-1800	
	1	$H + CH_3C \cdot HCI = C_2H_5 + CI$	2.45E+18	-1.60	5.00	600-1800	
	760	$H + CH_3C \cdot HCl = C_2H_5 + Cl$	7.02E+22	-2.81	9.52	600-1800	
	1	$H + CH_3C \cdot HCl = CH_3 + CH_2Cl$	1.16E+16	-0.55	5.47	600-1800	
	760	$H + CH_3C \cdot HCl = CH_3 + CH_2Cl$	6.90E+20	-1.85	9.93	600-1800	
	1	$H + CH_3C \cdot HCl = C_2H_4 + HCl$	2.31E+30	-5.13	6.73	600-1800	

^aSee Figure 11 for potential energy diagram. Units: A, bimolecular, cm³/(mol-s); unimolecular: 1/s. E_a , kcal/mol. ^b A_1 from 0.5 A_f for H + 2-C₄H₉. (1E+14, ref 11). ^cReverse (k_{-1}) from thermodynamics, A_1 , and microreversibility. ^d $E_a = \Delta H_r$; A_2 from thermodynamics, $A_{-2} = A_f$ for CH₃ + C₂H₅ (2E+13, ref 11), and microreversibility. ^e $E_a = \Delta H_r$; A_3 from thermodynamics, $A_{-3} = A_f$ for CH₃ + 2-C₃H₇ (1.6E+13, ref 11), and microreversibility. ^f $E_a = \Delta H_r$; A_3 from thermodynamics, $A_{-3} = A_f$ for CH₃ + 2-C₃H₇ (1.6E+13, ref 11), and microreversibility. ^f $E_a = \Delta H_r$; A_3 from thermodynamics, $A_{-3} = A_f$ for CH₃ + 2-C₃H₇ (1.6E+13, ref 11), and microreversibility. ^f $E_a = \Delta H_r$ + 35.5; $A_4 = 10E+13.2 \times 10E-4/4.6 \times 3$ (transition-state theory). ^gGeometric mean vibrational frequency from CPFIT (THERM) (ref 17) and C_p data. ^hLennard-Jones parameters estimated from C₂H₅Cl critical properties (ref 22).

TABLE VII: Species Thermodynamic Properties^a

-							-
	species	Δ <i>H</i> _f ° (298 K)	S° (298 K)	species	Δ <i>H</i> _f ° (298 K)	S° (298 K)	
	He	0.0	30.12	C ₂ H ₄	12.54	52.39	
	н	52.10	27.39	C_2H_5	28.36	57.90	
	H_2	0.0	31.21	C_2H_6	-20.24	54.85	
	CĨ	28.90	39.50	CH ₂ Cl	29.10	59.60	
	HCl	-22.06	44.64	C ₂ H ₃ Cl	5.00	63.08	
	CH,	35.12	46.38	C-H ₂ CH ₂ Cl	20.78	68.50	
	CH₄	-17.90	44.48	CH ₃ C·HCl	16.80	67.31	
	C ₂ H ₂	69.00	56.20	C ₂ H ₂ Cl	-26.83	66.03	

"Standard state for all species is gas at 298 K, 1 atm.



Figure 10. Calculated major intermediate and product species profiles.

 C_2H_3Cl conversion and subsequent product reaction pathways were dominated by reactions with H and possibly H_2 . A relative ranking of the dominant reactions in the system as a function of time indicated that the major reaction pathways during the 16-ms residence time are as shown in Figure 9. Concentration-time profiles for the major product species are presented in Figure 10. Consideration of these two figures yields insight into the formation of the observed products.

Atomic H addition to C_2H_3Cl forms primarily C_2H_4 and Cl, as discussed above. Production of C_2H_6 , CH₄, and HCl results from further reaction of these initial products. Reactions with H atoms dominate because of the excess H concentrations. Abstraction reactions of the various alkyl radicals in these systems with H₂ are insignificant due to the low temperature (300 K) and relatively high activation barriers for abstraction.²



Figure 11. Potential energy diagram for $H + CH_3C \cdot HCl$ combination.



Figure 12. Pressure dependence of the apparent bimolecular rate constants for $H + CH_3C$ -HCl combination.

The stabilized adduct CH₃C-HCl from eq 2 combines with H atom to form an activated C_2H_3Cl complex. This complex decomposes primarily to the lower energy exit channel of C_2H_4 + HCl.

$$H + CH_3C \cdot HCl \rightarrow [C_2H_5Cl]^* \rightarrow C_2H_4 + HCl \qquad (3)$$



Figure 13. Temperature dependence of the apparent bimolecular rate constants for $H + CH_3C+HCl$ combination.

The QRRK input parameters and calculated apparent rate constants for this combination reaction are given in Table VI, with energy level diagram in Figure 11. The rate constant dependence on pressure at 300 K is shown in Figure 12. The temperature dependence at 1 Torr is illustrated in Figure 13. Notice that stabilization is a minor pathway at 1 Torr and 300 K. The C_2H_4 + HCl product channel dominates over the C_2H_5 + Cl and CH₃ + CH₂Cl channels because its lower A factor is more than compensated by its low-energy barrier.

Atomic H adds to C_2H_4 to form an activated ethyl radical $[C_2H_5]^*$, which collisionally stabilizes.

$$H + C_2 H_4 \leftrightarrow [C_2 H_5]^* \xrightarrow{M} C_2 H_5$$
(4)

This reaction has been discussed by Westmoreland et al.¹⁶ As seen in Figure 9, the C_2H_4 concentration rises to a peak and then gradually falls.

The C₂H₅ concentration is 3-4 orders of magnitude lower than C₂H₄ because it readily combines with atomic H ($E_a = 0$) to form an activated [C₂H₆]^{*}. This complex rapidly decomposes to the lower energy products of CH₃ + CH₃.

$$H + C_2 H_5 \rightarrow [C_2 H_6]^* \rightarrow CH_3 + CH_3$$
 (5)

This system has been discussed, from the point of view of CH_3 + CH_3 , by Dean and Westmoreland.¹⁹ The large preexponential A factor associated with the CH_3 leaving groups, and the exothermicity of the products relative to the reactants, drives the chemically activated decomposition of $[C_2H_6]^*$ to $CH_3 + CH_3$. Figure 10 shows that the CH_3 concentration rises to a maximum after 16 ms.

Atomic H combines with CH_3 to form an activated complex, which collisionally stabilizes to CH_4 . This accounts for the steady buildup of CH_4 as a major product under these conditions.

$$H + CH_3 \leftrightarrow [CH_4]^* \xrightarrow{M} CH_4$$
(6)

This system has been extensively studied.¹⁸ The apparent rate constant for stable CH_4 production at these conditions (1 Torr, 300 K, He bath gas) is only 0.05% of the high-pressure limit. The production rate of CH_4 , however, is sufficient to yield a steadily rising concentration, as seen in Figure 10.

Formation of the observed C_2H_6 product occurs primarily by the combination of two CH₃ groups. The activated complex $[C_2H_6]^*$ is collisionally stabilized to C_2H_6 .

$$CH_3 + CH_3 \rightarrow [C_2H_6]^* \xrightarrow{M} C_2H_6$$
 (7)

This reaction system has been studied by Dean and Westmoreland.¹⁹ At the conditions of interest here, stabilization dominates over the two product channels. The $H + C_2H_5$ channel is endothermic relative to the starting reactants. Figure 10 shows the C_2H_6 concentration steadily rising. Formation of C_2H_6 competes with CH_4 production for available CH_3 radicals. We have established here that the primary chlorine product from the reaction of H with C_2H_3Cl at 1 Torr and 300 K is Cl atom, not HCl. Therefore, secondary reactions of Cl must be considered. With the excess of H_2 present, the most important Cl reaction is

$$Cl + H_2 \leftrightarrow HCl + H$$
 (8)

In the current system, this reaction is essentially at equilibrium. For the conditions of Ahmed and Jones,⁶ where the initial molar concentration of H atom is in great excess relative to C_2H_3Cl , the only additional secondary Cl reaction of significance is abstraction of H from product C_2H_6 .

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5 \tag{9}$$

This reaction has a higher A factor and lower activation energy (see Table III) than the similar abstraction from CH_4 . In addition, the abstraction from CH_4 is 2 kcal/mol endothermic, while the abstraction from C_2H_6 is 2.4 kcal/mol exothermic.

Experimental Approach for Identification of Pathways. At 300 K and 1 Torr, the immediate products from ipso addition of H to C_2H_3Cl are C_2H_4 and Cl. Through relatively rapid reaction with H_2 , the Cl product is converted to HCl. The major immediate products from nonipso addition (after isomerization) are the same. Therefore, it would appear difficult to experimentally differentiate between the these two pathways and verify the aforementioned claims.

Table V shows that 26% of the C_2H_3Cl direct consumption by H occurs by the nonipso addition/stabilization to CH_3CH ·Cl channel. This stabilized adduct then combines with H to produce an activated C_2H_3Cl , which rapidly decomposes to C_2H_4 + HCl.

At higher pressures, more of the $C_2H_5Cl^*$ complex will collisionally stabilize. This is the only route to produce C_2H_5Cl . Therefore, an experiment which monitors the concentration of C_2H_5Cl as a function of pressure will provide a means to differentiate between ipso and nonipso addition by H to C_2H_3Cl .

Effect of ΔH_f of C_2H_3 . There has been a controversy over the heat of formation of the C_2H_3 radical. Values have ranged from a low of 63 kcal/mol²⁰ to a high of 71 kcal/mol.²¹ An value of 69 kcal/mol was assumed in this study.

Referring to the Evans-Polanyi plot in Figure 7, the lower value of $\Delta H_{\rm f}$ for C₂H₃ would have resulted in an estimated $E_{\rm a}$ for abstraction (H + C₂H₃Cl = HCl + C₂H₃) of 9 kcal/mol. This value is still too high to allow abstraction to account for any of the C₂H₃Cl conversion by H at 300 K.

Barrier for Ipso Addition of H to C_2H_3Cl **.** Recent experimental results in our laboratories²⁴ suggest that the barriers for H addition to chloro-olefins might be 1–1.5 kcal/mol lower than those of Tsang.¹³ This slightly lower barrier has a negligible effect on our calculations at room temperature. At higher temperatures, the reaction pathway of H + C_2H_3Cl to C_2H_4 + Cl would be slightly accelerated.

Some insight into the different energies of activation for H atom attack on the carbons ipso and nonipso to the Cl in C_2H_3Cl , 5.8 and 2.9 kcal/mol, respectively, may come from analysis of the product radical C_2H_4Cl . Attack at the ipso position (E_a of 5.8 kcal/mol) results in C·H₂CH₂Cl^{*} complex, which experiences very little stabilization relative to the analogous ethyl radical CH₂CH₃. We assign the H–CH₂CH₂Cl bond energy of 100 kcal/mol, which represents a resonance stabilization of less than 1 kcal/mol relative to the H–CH₂CH₃ bond energy of 100.7 kcal/mol.

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Nonipso attack results in the $CH_3C \cdot HCl^*$ complex, which is significantly stabilized by the Cl atom on that carbon due to 5.0 kcal/mol of resonance stabilization energy (Mitokawa and Roux;25 Roux and Soloman²⁶). Thus the CH_3C ·HCl radical is some 4 kcal/mol lower in enthalpy than the $C \cdot H_2 C H_2 C l$ isomer.

We point out that, because the ipso addition barrier is 5.8 kcal/mol, this channel is not important at the temperatures of the experimental data we are matching. Our results would be similar for a higher barrier, but we feel it is warranted to recommend the 5.8 kcal/mol value for use in modeling and other calculations. As discussed earlier, this value comes from analysis of extensive literature measurements on H addition to C_2H_4 , and experiments by Tsang¹⁴ on H addition to C_2Cl_4 , and is strongly supported by theoretical calculations of Schlegle and Sosa.¹⁵ The rate constants for addition to the nonipso olefin carbon in C_2H_3Cl and for the H shift are, on the other hand, of very high sensitivity in our model comparison to the low-pressure experimental data. If the H shift rate constant were much lower (i.e., a higher barrier),

our model could not match the data because a relatively significant fraction of the CH₃C·HCl^{*} complex would dissociate back to reactants rather than be stabilized.

Conclusions

The key conclusions to be drawn from this study are as follows: At 300 K, the conversion of C_2H_3Cl by H occurs by addition and not by abstraction of Cl.

Nonipso addition is favored over ipso addition in this case. In the nonipso sequence, a chemically activated isomerization (1,2 hydrogen atom shift) occurs before adduct decomposition to the lower energy C_2H_4 + Cl exit channel.

At 300 K and 1 Torr, the chemically activated adduct is formed by nonipso addition and primarily decomposes to the $C_2H_4 + Cl$ lower energy exit channel. The adduct stabilization channel is also important, leading to the same final products in this hydrogen-rich environment.

Experiments at pressures in excess of 1 Torr with analysis for stable C_2H_5Cl might yield data to verify the ratio between stabilization and 1,2 H shift in the nonipso attack.

Registry No. H, 12385-13-6; H₂C=CHCl, 75-01-4.

Dual Laser Excitation of a Photochromic System: Application to DODCI

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A technique based on a combination of pump-and-probe fluorescence and absorption detection was developed in order to obtain the emission parameters of the photoisomeric (P) species of dyes with noncompletely overlapped absorption spectra of P and the starting species (N). Near total population transfer to the ground state of P was achieved using a continuous wave high-fluence pump laser. A pulsed laser probed this population in its absorption region in such a way that the pulsed emission corresponded to fluorescence from P. Absorption measurements allowed us to follow the P population and to establish its relationship with pump fluence and wavelength. The direct monitoring of the P concentration increased the accuracy of the previously reported values for several photophysical parameters. Temperature-dependent fluorescence quantum yield and lifetime, emission spectrum, and Arrhenius parameters of the nonradiative decay processes of P from 3,3'-diethyloxadicarbocyanine iodide (DODCI) are given. The mechanism for the direct transformation between N and P through the singlet excited states of DODCI is re-evaluated.

Introduction

Photoisomerization processes of cyanine dyes have been analyzed through several techniques: flash photolysis,^{1,2} picosecond spectroscopy,³ photoacoustics,⁴ thermal grating,⁵ laser saturated absorption⁶ and fluorescence,⁷ absorption and emission spectroscopy with conventional sources,8 etc. These techniques exhibit a common drawback in the determination of the kinetic parameters of the photoisomeric species P in an indirect way, using a photoisomerization model for the simultaneous fit of several parameters. This procedure leads to an inherent lack of precision. While it can be used for either totally overlapped absorption-emission spectra (DTDCI, merocyanine 540, etc.) or partially overlapped spectra (DODCI, HITCI, etc.), it is only with using time-resolved picosecond spectroscopy that the different contributions can be directly obtained.

Some spectroscopic properties of P in photoisomerizable dyes with partially overlapped spectra have been reported previously.9,10 These experiments were based on continuous wave (CW) and pulsed excitation of the sample. The CW laser, tuned at the absorption wavelength of the normal (N) ground-state species, produced a stationary population of the P ground state while the second laser (pulsed) probed this population. The pulsed fluorescence arose from P free from interference from the N emission.

In the present work, the measurements were performed at high pump fluence for which the photoequilibrium populations of all levels involved are shown to be independent of this pump fluence. Under this condition (saturation), the analysis of the results is

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