Reactions between chlorine atom and acetylene in solid para-hydrogen: Infrared spectrum of the 1-chloroethyl radical

Barbara Golec and Yuan-Pern Lee

Citation: The Journal of Chemical Physics 135, 174302 (2011); doi: 10.1063/1.3653988
View online: http://dx.doi.org/10.1063/1.3653988
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/135/17?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Infrared absorption of 3-propenonyl (CH2CHCO) radical generated upon photolysis of acryloyl chloride [CH2CHC(O)Cl] in solid para-H2

Infrared identification of the -complex of Cl-C6H6 in the reaction of chlorine atom and benzene in solid para-hydrogen

Reactions between atomic chlorine and pyridine in solid para-hydrogen: Infrared spectrum of the 1-chloropyridinyl (C5H5NCl) radical

Infrared absorption of trans-1-chloromethylallyl and trans-1-methylallyl radicals produced in photochemical reactions of trans-1,3-butadiene and C2 in solid para-hydrogen

Reaction of vinyl radical with oxygen: A matrix isolation infrared spectroscopic and theoretical study
Reactions between chlorine atom and acetylene in solid para-hydrogen: Infrared spectrum of the 1-chloroethyl radical

Barbara Golec1 and Yuan-Pern Lee1,2,a)
1Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan
2Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan

(Received 5 August 2011; accepted 1 October 2011; published online 2 November 2011)

We applied infrared matrix isolation spectroscopy to investigate the reactions between Cl atom and acetylene (C2H2) in a para-hydrogen (p-H2) matrix at 3.2 K; Cl was produced via photodissociation at 365 nm of matrix-isolated Cl2 in situ. The 1-chloroethyl radical (·CHClCH3) and chloroethene (C2H3Cl) are identified as the main products of the reaction Cl + C2H2 in solid p-H2. IR absorption lines at 738.2, 1027.6, 1283.4, 1377.1, 1426.6, 1442.6, and 2861.2 cm−1 are assigned to the 1-chloroethyl radical. For the reaction of Cl + C2D2, lines due to the ·CDCIC2H3D radical and trans-CHDCDCl are observed; the former likely has a syn-conformation. These assignments are based on comparison of observed vibrational wavenumbers and 13C- and D-isotopic shifts with those predicted with the B3LYP/aug-cc-pVDZ and MP2/aug-cc-pVDZ methods. Our observation indicates that the primary addition product of Cl + C2H2, 2-chlorovinyl (·CHCHCl) reacts readily with a neighboring p-H2 molecule to form ·CHCHCl2 and C2H2Cl. Observation of ·CDCIC2H3D and trans-CHDCDCl from Cl + C2D2 further supports this conclusion. Although the reactivity of p-H2 appears to be a disadvantage for making highly reactive free radicals in solid p-H2, the formation of 1-chloroethyl radical indicates that this secondary reaction might be advantageous in producing radicals that are difficult to prepare from simple photolysis or bimolecular reactions in situ. © 2011 American Institute of Physics. [doi:10.1063/1.3653988]

I. INTRODUCTION

The reaction between Cl2 and acetylene (ethyne, C2H2) is a prototype for addition reactions of halogen to carbon–carbon triple bonds in organic chemistry. The reaction is believed to proceed via a radical mechanism in which addition of a Cl atom to the triple bond initiates the reaction.1 The reaction of Cl atom with C2H2 is reported to play an important role in their removal from the marine atmosphere and the polar troposphere;2–4 the reaction serves also as a sink of Cl atoms in the stratosphere.5–7

The Cl + C2H2 reaction has been the subject of numerous experimental4,5–14 and theoretical investigations.1,10,15 These studies indicate that two initial processes, the addition of the Cl atom to C2H2 to form the 2-chlorovinyl radical (·CHCHCl) and the abstraction of an H atom of C2H2 to form the ethynyl radical (·CCH) and HCl, are possible for this reaction. The branching ratio of these two channels depends on pressure and temperature. The radical products subsequently undergo further reactions to form stable molecular products such as dichloroethene and higher chlorohydrocarbons. The infrared (IR) absorption experiments reported by Zhu and Yarwood9 indicate that the photoliorination of gaseous C2H2 in N2 produces cis-CHCHICHCl (16%) and trans-CHCHICHCl (84%).

Quantum-chemical calculations indicate that the addition reaction of Cl + C2H2 proceeds via a Cl-C2H2 complex of C2v symmetry to form the 2-chlorovinyl radical, ·CHCHCl, with an exothermicity of 57–73 kJ mol−1. The 2-chlorovinyl radical is predicted to have two isomers: trans-CHCHCl is more stable than cis-CHCHCl by ∼5 kJ mol−1 and the barrier for converting cis-CHCHCl to trans-CHCHCl is ∼16 kJ mol−1.15 The spectral identification of the 2-chlorovinyl radical remains unreported.

For reactions of C2H2 with small atoms such as H or F, IR absorption of the radical products of the addition reactions, ·CHCH3 (see Ref. 16) and ·CHCHF17,18 isolated in noble-gas matrices were identified. These species were generated in noble-gas matrices via annealing-induced reactions or via co-deposition of C2H2 and F atoms produced in a microwave discharge. Preceding work indicates that the cage effects associated with conventional Ar or Ne matrices pose some limitation to study the reactions of Cl or Br atoms produced from ultraviolet (UV) photolysis of Cl2 or Br2 in situ. The Cl or Br atoms produced in these matrices cannot escape the original matrix cage easily; consequently the observed products typically involve the reaction of both halogen atoms.19,20

The use of solid para-hydrogen (p-H2) as a matrix host has generated considerable interest in recent years because of the unique properties associated with this quantum solid.21–24 The diminished matrix cage effect makes feasible investigations of free radicals via direct photolysis of precursors25–27 or bimolecular reactions induced from photolysis in situ.28–31 RAston and Anderson32 employed laser emission at 355 nm to photodissociate Cl2 trapped in solid p-H2 at 2 K and produced isolated Cl atoms. It is thus expected that

---

a)Author to whom correspondence should be addressed. Electronic mail: yplee@mail.nctu.edu.tw. Fax: 886-3-5713491.
reaction of Cl with other small molecules might produce free radicals that are difficult to produce in noble-gas matrices. Our research group has demonstrated that irradiation of a Cl₂/CS₂/p-H₂ matrix with UV light at 340 nm results in reaction products containing only a single chlorine atom: CISCs, CICS, and CISC.28 Similarly, UV radiation of matrices Cl₂/C₂H₄/p-H₂ and Cl₂/propane/p-H₂ with light at 365 nm produces 2-chloroethyl (·CH₂CH₂CH₂Cl)²⁹ and 2-chloropropyl (·CH₂CH_CH₂Cl) radicals,³⁰ respectively.

In this paper, we report IR absorption spectra of the reaction products resulting from UV irradiation of p-H₂ matrices containing Cl₂ and C₂H₂ (or ¹³C₂H₂, C₂D₂); the addition product ·CHCHCl reacts readily with neighboring p-H₂ to form 1-chloroethyl radicals (·CH₃CH₂Cl) and chloroethene (C₂H₃Cl) as major products.

II. EXPERIMENTS

A gold-plated copper block, maintained at 3.2 K, served as both a cold substrate for the matrix sample and a mirror to reflect the incident IR beam to the detector.²⁶,³³ The low temperature was achieved with a closed-cycle refrigerator system (Janis RKD-415). Typically, gaseous mixtures of C₂H₂/p-H₂ and Cl₂/p-H₂ were co-deposited over a period of 5–8 h at flow rates of 7–8 mmol h⁻¹. The mixing ratio of the C₂H₂/p-H₂ mixture was 1/1000–1/2000, and that of Cl₂/p-H₂ mixture was 1/600–1/4000.

IR absorption spectra were recorded with a Fourier-transform IR spectrometer (Bomem, DA8) equipped with a KBr beam splitter and a HgCdTe detector cooled to 77 K to cover the spectral range 500–5000 cm⁻¹. Typically, 500 scans at 0.25 cm⁻¹ resolution were co-added at each stage of the experiment. All spectra were recorded at 3.2 K. Excitation of the solid p-H₂ with IR light in the range 4000–5000 cm⁻¹ induces reactions of Cl atoms with p-H₂ to form HCl.³⁴,³⁵ In our experiments when Cl atoms were present in the p-H₂ matrix, an IR filter with a cutoff wavelength at 2.4 μm (Andover Co.) was therefore used when recording the IR spectra to avoid the reaction of Cl + H₂.

In some experiments, after the initial co-deposition of the Cl₂/p-H₂ and C₂H₂/p-H₂ mixtures, the matrix was annealed at 4.3 K for up to 0.5 h to enhance production of the complex between Cl₂ and C₂H₂. To produce Cl atoms for reaction with C₂H₂, the Cl₂/C₂H₂/p-H₂ matrices were irradiated with light at 365 ± 10 nm from a light-emitting diode (Holle UV Technology, 375 mW) for 2–5 h. Following the photolysis at 365 nm, the matrix was sometimes annealed to 4.3 K to induce further reaction. Secondary photolysis was performed using one or more of the following light sources: a globar with a bandpass filter passing 3870–4980 cm⁻¹ (W02296-7, OCLI Products), a low-pressure Hg lamp (Pen-Ray lamp, UVP) with or without a bandpass filter passing 254 ± 10 nm (ESCO Products), and a Zn lamp without a filter. The increase or decrease in line intensities in different extent observed after photolysis enables us to separate observed lines into various groups that are attributable to various products.

p-H₂ was produced by catalytic conversion at low temperature in which normal H₂ gas (99.9999%, Scott Specialty Gases) was passed through a copper coil filled with a hydrated iron (III) oxide catalyst (catalyst grade, 30–50 mesh, Sigma-Aldrich) that was cooled with a closed-cycle refrigerator (Advanced Research Systems, DE204AF). Before entering the coil containing the catalyst, the H₂ gas was passed through a trap cooled to 77 K. The efficiency of the conversion is controlled by the temperature of the catalyst, which was typically 13–14 K in these experiments. At this temperature, the mixing ratio of o-H₂ is less than 100 ppm according to the Boltzmann distribution.

III. RESULTS

A. Calculations on the C₂H₂-Cl₂ complex, 2-chlorovinyl (·CHCHCl), and 1-chloroethyl (·CH₂CH₂Cl) radicals

The equilibrium geometries, vibrational wavenumbers, IR intensities, and energies were calculated with the GAUSSIAN 09 program.³⁶ Our calculations are based on B3LYP density-functional theory and the second-order Møller-Plesset perturbation theory (MP2).³⁵ Dunning’s correlation-consistent polarized-valence double-zeta basis set augmented with s, p, d, and f functions (aug-cc-pVDZ) (Ref. 40) was used in both methods. Algebraic first derivatives were utilized in geometry optimization, and harmonic vibrational wavenumbers were calculated analytically at each stationary point. The anharmonic effects were calculated by second-order perturbation approach using effective finite difference evaluation of the third and semidiagonal fourth derivatives.

1. The C₂H₂-Cl₂ complex

The calculations predicted that the most stable structure of C₂H₂-Cl₂ is a T-shaped br-αα complex.⁴¹–⁴⁴ The structural parameters predicted with the B3LYP/aug-cc-pVDZ method are shown in Fig. 1(a), and those predicted with the MP2/cc-pVDZ method are listed parenthetically. These structures are consistent with literature values. At the B3LYP/aug-cc-pVDZ level of theory, harmonic vibrational wavenumbers of C₂H₂-Cl₂ are predicted at 3518, 3414, 2052, 740, 727, 571, 556, and 480 cm⁻¹, whereas anharmonic vibrational wavenumbers are predicted at 3373, 3279, 2020, 758, 767, 772, and 481 cm⁻¹. At the MP2/aug-cc-pVDZ level of theory, these values become 3512, 3424, 1938, 712, 701, 415, 394, and 512 cm⁻¹. Predicted harmonic and anharmonic vibrational wavenumbers and IR intensities of C₂H₂-Cl₂, ¹³C₂H₂-Cl₂, and C₂D₂-Cl₂ are compared with the experimental values in Table I.

2. 2-Chlorovinyl (·CHCHCl) and 1-chloroethyl (·CH₂CH₂Cl) radicals

The 1-chloroethyl (·CCICH₂) radical is predicted to be the most stable isomer of chlorovinyl radicals, with its energy smaller than that of trans-CHCHCl by 13.9, 12.7, and 12.4 kJ mol⁻¹, respectively, according to the B3LYP/aug-cc-pVDZ, MP2/aug-cc-pVDZ, and CCSD(T)/aug-cc-pVDZ/CCSD(6-31G(d,p)) methods. However, 1-chlorovinyl cannot be produced directly from Cl + C₂H₂. Isomerization from
The geometries of the 1-chloroethyl radical computed in this work at the B3LYP/aug-cc-pVDZ method are listed in Table III. Those of the three conformers of ·CDCICH2D and two of ·CHDCHDCI are listed in Table S1, see supplementary material.46

B. Formation of the C2H2-Cl2 complex in solid p-H2

1. Experiments of Cl2 + C2H2 in natural abundance

The infrared spectrum of C2H2 in p-H2 at 3.2 K in the spectral region between 500 and 4000 cm⁻¹ is characterized by a series of lines with the most intense feature (ν3) at 733.8 cm⁻¹ and weaker ones at 1331.6 (ν4 + ν5) cm⁻¹, 3279.4 (ν3) cm⁻¹, and 3294.4 (ν2 + ν4 + ν5) cm⁻¹, in agreement with literature spectra of C2H2 in a supersonic jet47 and isolated in Ar48 and Kr.49 In a more dilute C2H2 sample in solid p-H2, the line at 733.8 cm⁻¹ shifts to 738.5 cm⁻¹, as reported previously.47

When the p-H2 matrix was doped with both C2H2 and Cl2 a set of new lines unobserved in the C2H2/p-H2 matrix appears; their intensity increases upon annealing to 4.3 K. These new features at 3276.0, 1968.8, 741.7, 732.2, 539.4, and 532.2 cm⁻¹ are assigned to C2H2-Cl2 complexes, consistent with lines at 3277, 1972, 776, and 527 cm⁻¹ reported for C2H2-Cl isolated in solid Ar.41 Laursen and Pimentel42 reported lines with similar wavenumbers for C2H2-Cl2 upon irradiation at 237 nm of cis and trans-1,2-C2H2Cl2 in solid Xe, and at 239 nm of cis-1,2-C2H2Cl2 in isolated solid Xe,43 as listed in Table I.

These lines are consistent with theoretical predictions of vibrational wavenumbers of C2H2-Cl2,44 as listed in Table I; predicted anharmonic vibrational wavenumbers fit better. Activation of the originally forbidden C≡C stretching mode near 1968.8 cm⁻¹ and the Cl−Cl stretching modes near 539.4 and 532.3 cm⁻¹ is due to the interaction between Cl2 and C2H2.

2. Experiments with the 13C- and D-isotopic species

The vibrational wavenumbers of 13C2H2-Cl and C2D2-Cl2 observed experimentally and calculated with the B3LYP and MP2 methods are also summarized in Table I.
Absorption lines of the $^{13}$C$_2$H$_2$-Cl$_2$ complex are similar to those of $^{12}$C$_2$H$_2$-Cl$_2$ except that some lines are slightly redshifted. The most intense line of C$_2$H$_2$-Cl$_2$ shifts from 741.7 to 739.7 cm$^{-1}$ with a $^{13}$C-isotopic ratio of 739.7/741.7 = 0.9973, defined as the ratio of the vibrational wavenumber of isotopic species to that of the natural species. This ratio is in agreement with the theoretical value of 759.3/763.3 = 0.9948 according to anharmonic vibrational wavenumbers predicted with the B3LYP method. The largest isotopic shift was observed for the C≡C stretching mode with the line of $^{12}$C$_2$H$_2$-Cl$_2$ at 1968.8 cm$^{-1}$ shifts to 1759.4 cm$^{-1}$ for C$_2$D$_2$-Cl$_2$. The D-isotopic shift of 209.4 cm$^{-1}$ agrees satisfactorily with the predicted value of 229.5 cm$^{-1}$.

### C. Photolysis of Cl$_2$/C$_2$H$_2$/p-H$_2$ matrices

#### 1. Experiments of Cl$_2$ + C$_2$H$_2$ in natural abundance

Upon irradiation of a Cl$_2$/C$_2$H$_2$/p-H$_2$ matrix with light at 365 nm, the intensity of IR features due to C$_2$H$_2$ and C$_2$H$_2$-Cl$_2$ complexes decreased, and new features in several groups appeared. These new features are expected to belong to the reaction products between Cl atoms, produced via photolysis of Cl$_2$, and C$_2$H$_2$. A difference spectrum obtained on...
subtracting the spectrum of a Cl2/C2H2/p-H2 (1/2/6000) matrix, deposited at 3.2 K for 7 h, from the spectrum recorded after irradiation at 365 nm for 5 h is presented in Fig. 3(a); lines pointing upwards indicate production. A difference spectrum obtained on subtracting the spectrum of a Cl2/C2H2/13C2H2 (1/1/2000) matrix, deposited at 3.2 K for 5 h and annealed at 4.3 K for 0.5 h, from the spectrum recorded after irradiation at 365 nm for 3 h is presented in Fig. 3(b). The difference spectrum obtained after annealing of this irradiated matrix at 4.3 K for 0.5 h is shown in Fig. 3(c).

The intense features marked as group X in Fig. 3(a) and listed in Table III appeared after irradiation of the matrix at 365 nm, but their intensities decreased slightly when the matrix was subsequently irradiated with IR light, as shown in Fig. 3(d). Weak lines at 3100.8, 2970.2, 2902.3 (all marked “X”), and 1106.0 cm⁻¹ (not shown) might be associated also with group X. This behavior indicates that these features are likely associated with an unstable species that reacts with vibrationally excited H2 or H atoms. These lines of group X are assigned to the 1-chloroethyl (−CHClCH3) radical, to be discussed in Sec. IV A.

The lines of group B, as shown in Fig. 3(b) and listed in Table V, appeared after irradiation of the Cl2/C2H2/p-H2 (1/1/2000) matrix at 365 nm but their intensities are much smaller in a matrix with more diluted Cl2, for which only lines at 1058.7 and 702.8 cm⁻¹ are clearly visible in Fig. 3(a); their intensities remained nearly unchanged upon further IR irradiation. These features are readily assigned to 1,1-dichloroethane, CHCl2CH3, based on the literature spectra of this compound and the observation of enhanced intensity of lines in this group when an increased mixing ratio of Cl2 in the Cl2/C2H2/p-H2 matrix was used.

Weak lines of group C at 1440.0 and 948.4 cm⁻¹ are assigned to ν7 and ν12 modes of C2H4, respectively, according to literature values29, 51 and our experiments with C2H4/p-H2. As shown in Fig. 3(d), the intensities of these features increased greatly and additional lines in this group appeared after IR irradiation.

Upon IR irradiation, intense lines due to HCl at 2894.2 and 2892.1 cm⁻¹ increased substantially.34, 35 Weaker lines indicated as group D in Fig. 3(d) and listed in Table V appeared. These features are clearly due to chloroethane (C2H5Cl).52 We observed in Fig. 3(d) also small proportions of C2H4 radicals (group F), a C2H2−HCl complex (group C),53, 54 and C2H6 (group E), as listed in Table V.55

2. Experiments with the Cl2/p3C2H2/p-H2 matrix

In a few experiments, 13C2H2 was replaced with 13C2H2 and the Cl2/13C2H2/p-H2 matrices were irradiated at 365 nm following by IR irradiation at 3870–4980 cm⁻¹. A difference spectrum obtained on subtracting the spectrum of the

![FIG. 2. (a) Geometries of CHClCH3 predicted with the B3LYP/aug-cc-pVDD method. Corresponding values predicted with the MP2/aug-cc-pVDD method are listed in parentheses. Results predicted with the QCISD/6-31G(d,p) method (Ref. 45) are listed in brackets for comparison. Bond distances are in Å and angles are in degrees. (b) The dihedral angles of three conformers of CDCICH3.](Image 1)
TABLE III. Comparison of experimental wavenumbers (cm$^{-1}$) and relative IR intensities of group X (·CHClCH$_3$ and ·$^{13}$CHCl$^{13}$CH$_3$) in solid $p$-H$_2$ with harmonic vibrational wavenumbers and IR intensities predicted with the B3LYP/aug-cc-pVDZ and MP2/aug-cc-pVDZ methods.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$C-shift</td>
<td>·CHClCH$_3$</td>
<td>·$^{13}$CHCl$^{13}$CH$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_1$</td>
<td>3224.3 (12)$^a$</td>
<td>3254.6 (18)</td>
<td>3100.8? (18)</td>
<td>-10.7</td>
<td>-9.8</td>
</tr>
<tr>
<td>$v_2$</td>
<td>3105.0 (29)</td>
<td>3168.2 (20)</td>
<td>2902.3? (22)</td>
<td>-9.8</td>
<td>-12.8</td>
</tr>
<tr>
<td>$v_3$</td>
<td>3051.6 (34)</td>
<td>3124.5 (25)</td>
<td>2970.2? (23)</td>
<td>-1.7</td>
<td>-1.3</td>
</tr>
<tr>
<td>$v_4$</td>
<td>2977.3 (54)</td>
<td>3034.9 (38)</td>
<td>2861.2 (27)</td>
<td>-5.9</td>
<td>-3.8</td>
</tr>
<tr>
<td>$v_5$</td>
<td>1449.1 (7)</td>
<td>1470.1 (8)</td>
<td>1442.6 (5)</td>
<td>-1.7</td>
<td>-2.2</td>
</tr>
<tr>
<td>$v_6$</td>
<td>1426.8 (20)</td>
<td>1454.9 (23)</td>
<td>1426.6 (23)</td>
<td>-2.2</td>
<td>-2.5</td>
</tr>
<tr>
<td>$v_7$</td>
<td>1381.7 (17)</td>
<td>1393.5 (20)</td>
<td>1377.1 (25)</td>
<td>-11.7</td>
<td>-10.7</td>
</tr>
<tr>
<td>$v_8$</td>
<td>1283.4 (100)</td>
<td>1304.7 (100)</td>
<td>1283.4 (100)</td>
<td>-11.4</td>
<td>-11.1</td>
</tr>
<tr>
<td>$v_9$</td>
<td>1114.5 (12)</td>
<td>1133.2 (10)</td>
<td>1106.0? (6)</td>
<td>-31.3</td>
<td>-42.0</td>
</tr>
<tr>
<td>$v_{10}$</td>
<td>1025.0 (44)</td>
<td>1037.0 (45)</td>
<td>1027.6 (61)</td>
<td>-14.4</td>
<td>-14.7</td>
</tr>
<tr>
<td>$v_{11}$</td>
<td>980.7 (0)</td>
<td>997.8 (0)</td>
<td>-9.4</td>
<td>-9.4</td>
<td></td>
</tr>
<tr>
<td>$v_{12}$</td>
<td>719.5 (71)</td>
<td>744.5 (68)</td>
<td>738.2 (&gt;50)$^b$</td>
<td>-15.6</td>
<td>-15.0</td>
</tr>
<tr>
<td>$v_{13}$</td>
<td>360.8 (22)</td>
<td>472.9 (65)</td>
<td>-5.0</td>
<td>-5.0</td>
<td></td>
</tr>
<tr>
<td>$v_{14}$</td>
<td>285.3 (54)</td>
<td>336.1 (5)</td>
<td>-1.5</td>
<td>-1.5</td>
<td></td>
</tr>
<tr>
<td>$v_{15}$</td>
<td>142.0 (5)</td>
<td>182.4 (0)</td>
<td>+1.6</td>
<td>+1.6</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Relative IR intensities normalized to the most intense line. Intensities of lines near 1283 cm$^{-1}$ for CHClCH$_3$ are 41 (B3LYP) and 40 (MP2) km mol$^{-1}$. Those near 1272 cm$^{-1}$ for $^{13}$CHCl$^{13}$CH$_3$ are 36 (B3LYP) and 35 (MP2) km mol$^{-1}$, respectively.

$^b$The intensity is difficult to determine because of severe overlap with other lines.

Cl$_2$/$^{13}$C$_2$H$_2$/p-H$_2$ (1/1/3/4000) matrix, deposited at 3.2 K for 8.5 h, from the spectrum recorded after irradiation at 365 nm for 3 h is presented in Fig. 4(a). A similar spectrum obtained on subtracting the spectrum of the Cl$_2$/$^{13}$C$_2$H$_2$/p-H$_2$ (1/1/2000) matrix, deposited at 3.2 K for 7 h, from the spectrum recorded after irradiation at 365 nm for 3 h is presented in Fig. 4(b).

Lines in group A, assigned to $^{13}$C$_2$H$_3$Cl, were identified at 3073.9, 1561.7, 1356.8, 1274.9, 1016.9, 941.1, 886.9, 703.0, 697.5, and 612.6 cm$^{-1}$, as listed in Table V and marked as “A” in Fig. 4(a). The largest isotopic shift was observed for the C = C stretching mode with a shift of 48.1 cm$^{-1}$ and an isotopic ratio of 1561.7/1609.8 = 0.9701, in agreement with values 55.1 cm$^{-1}$ and 1608.2/1663.3 = 0.9669 according to harmonic vibrational wavenumbers predicted with the B3LYP method. A comparison of vibrational wavenumbers observed for C$_2$H$_3$Cl and $^{13}$C$_2$H$_3$Cl and the harmonic vibrational wavenumbers predicted with B3LYP is listed in Table S2, see supplementary material.46

Lines in group X were observed at 2857.4, 1424.1, 1366.4, 1272.3, 1012.9, 723.2, and 718.1 cm$^{-1}$, as listed in Table III and marked as “X” in Fig. 4(a). The line at 723.2 cm$^{-1}$, shifted from 738.2 cm$^{-1}$ of the $^{12}$C-species, possesses the largest isotopic shift, with an isotopic ratio of 723.2/738.2 = 0.9797.

Vibrational wavenumbers of other minor lines of known species observed in the Cl$_2$/$^{13}$C$_2$H$_2$/p-H$_2$ experiments are listed in Table V.
Possible deuterated isomers of chloroethene produced from the trans- of D atoms. Comparison of line positions and relative IR intensities in nm of the Cl2/C2D2/p-H2 matrix and after further irradiation in the 3870–4980 cm−1 region are shown in Figs. 5(a) and 5(b), respectively. Lines in group A shifted to 1560.6, 1268.1, 993.9, 851.5, 697.6, and 692.0 cm−1 (group A1 in Table V and Fig. 5(a)). Possible deuterated isomers of chloroethene produced from Cl + C2D2 are trans-CHDCDCl and cis-CHDCDCl, in which the trans- and cis-conformations refer to the relative position of D atoms. Comparison of line positions and relative IR intensities of trans-CHDCDCl, cis-CHDCDCl, and CHCICD2 with experimental observations is available from Table S3 in the supplementary material. Lines in group A matches better with those predicted for trans-CHDCDCl, to be discussed in Sec. IV B 2.

The lines in group X shifted to 1418.2, 1286.1, 1246.6, 1121.4, 1045.8, 915.2, 816.8, 814.8, 668.5, and 665.4 cm−1, as listed in Table IV. They are assigned to · CDCICD2, to be discussed in Sec. IV B.

As a result of secondary IR irradiation of the 365-nm irradiated Cl2/C2D2/p-H2 matrix, lines due to the formation of minor products cis-CHDCDCl (group A2), syn-CH3DCHDCl (group D3), anti-CH3DCHDCl (group D3), cis-CHDCDCl (group C3), trans-CHDCDCl (group C3), trans-CHDCDCl-HCl complex (group C3), and C2H3D (group C1) were observed, as indicated in Fig. 5(b) with observed wavenumbers listed in Table V. A comparison with calculated vibrational wavenumbers and IR intensities of these products is listed in Table S4, available from the supplementary material.

IV. DISCUSSION

A. Assignments of lines in group X observed in the Cl2/C2H2/p-H2 and Cl2/13C2H2/p-H2 experiments to the 1-chloroethyl (· CHCICD2) radical

The expected carrier of the new lines in group X is the product of the Cl + C2H2 addition reaction, cis- or trans-CHCHCl, or their secondary reaction products, but observed line positions and relative IR intensities do not match with those predicted for cis- and trans-CHCHCl, as listed in Table II. The intense IR lines of trans-CHCHCl are predicted at 1637, 826, 783, and 639 cm−1, and those of cis-CHCHCl are at 1635, 821, 618, and 578 cm−1, both inconsistent with our observation. These features of group X can neither be ascribed to the products of a H-abstraction channel, the ethynyl radical (C2H) or the C2H-HCl complex. Vibrational wavenumbers of C2H isolated in a Ne matrix are reported to be 3293.3 and 1835.5 cm−1, inconsistent with our observation.

From Fig. 3(d), we observed that lines in group X diminished upon secondary IR irradiation, whereas those of C2H3Cl increased. We reasonably assume that, upon secondary IR irradiation of the matrix, this species reacts with H or H2 to form C2H3Cl. The most likely candidate for this unstable carrier of lines in group X is thus the C2H3Cl radical. Two isomers of C2H3Cl are stable: 1-chloroethyl (· CHCICD2) and 2-chloroethyl (· CH2CH2Cl) radicals. These radicals are expected to react readily with H or H2 to form C2H3Cl upon irradiation of the p-H2 matrix with IR light.

Our group reported the infrared spectra of 2-chloroethyl radicals observed upon irradiation at 365 nm of a matrix containing Cl2 and C2H2:29 lines at 3129.3, 3041.1, 1228.0, 1069.9, 664.0, and 562.1 cm−1 are assigned to · CH2CH2Cl, with the line at 664.0 cm−1 being the most intense. Observed lines in group X do not match with those of the 2-chloroethyl radical.

The three most intense IR lines under 2000 cm−1 predicted for the 1-chloroethyl (· CHCICD2) radical with the B3LYP method are at 1283, 1025, and 720 cm−1 (Table III). They are assigned to the CH bending, CH3 rocking, and C–Cl stretching modes, respectively. These values fit satisfactorily with the three most intense lines at 1283.4, 1027.6, and 738.2 cm−1 observed in group X, as shown in Figs. 3(a) and 3(b). Other lines of group X at 2861.2, 1442.6, 1426.6, and 1377.1 cm−1 also fit with lines predicted near 2977, 1449, 1427, and 1382 cm−1 with acceptable relative intensities. Weak lines at 3100.8, 2970.2, 2902.3, and 1106.0 cm−1 might be associated also with group X; the wavenumbers are consistent with harmonic vibrational wavenumbers predicted near 3224, 3105, 3052, and 1115 cm−1, as compared in Table III.

For the 13C-substituted species, these three most intense lines shift to 1272.3 cm−1 (shift Δ = −11.1), 1012.9 cm−1 (Δ = −14.7), and 723.2 cm−1 (Δ = −15.0 cm−1), respectively.

### Table IV. Comparison of harmonic vibrational wavenumbers (in cm−1) and IR intensities of three conformers of · CDCICD2 predicted with the B3LYP/aug-cc-pVDZ method with experimental wavenumbers and relative intensities in solid p-H2.

<table>
<thead>
<tr>
<th>Mode</th>
<th>syn-</th>
<th>anti-</th>
<th>syn-</th>
<th>anti-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CDCICD2</td>
<td>CDCICD2</td>
<td>CDCICD2</td>
<td>p-H2</td>
</tr>
<tr>
<td>v1</td>
<td>3062.2 (40)</td>
<td>3039.3 (23)</td>
<td>3103.9 (24)</td>
<td></td>
</tr>
<tr>
<td>v2</td>
<td>2985.6 (69)</td>
<td>2983.5 (38)</td>
<td>3042.8 (25)</td>
<td></td>
</tr>
<tr>
<td>v3</td>
<td>2377.1 (10)</td>
<td>2376.8 (5)</td>
<td>2376.8 (6)</td>
<td></td>
</tr>
<tr>
<td>v4</td>
<td>2262.3 (18)</td>
<td>2240.1 (11)</td>
<td>2186.2 (22)</td>
<td></td>
</tr>
<tr>
<td>v5</td>
<td>1454.4 (20)</td>
<td>1415.9 (5)</td>
<td>1419.3 (13)</td>
<td>1418.2 (26)</td>
</tr>
<tr>
<td>v6</td>
<td>1289.0 (53)</td>
<td>1285.0 (11)</td>
<td>1268.6 (8)</td>
<td>1266.1 (10)</td>
</tr>
<tr>
<td>v7</td>
<td>1245.5 (13)</td>
<td>1263.8 (5)</td>
<td>1278.0 (11)</td>
<td>1266.6 (7)</td>
</tr>
<tr>
<td>v8</td>
<td>1128.6 (100)</td>
<td>1148.4 (100)</td>
<td>1139.4 (100)</td>
<td>1121.4 (100)</td>
</tr>
<tr>
<td>v9</td>
<td>1011.9 (70)</td>
<td>1004.9 (9)</td>
<td>1038.2 (17)</td>
<td>1045.8 (~8)</td>
</tr>
<tr>
<td>v10</td>
<td>929.4 (17)</td>
<td>870.7 (1)</td>
<td>847.9 (1)</td>
<td>915.2 (5)</td>
</tr>
<tr>
<td>v11</td>
<td>810.5 (20)</td>
<td>821.5 (1)</td>
<td>807.3 (1)</td>
<td>816.8 (14)</td>
</tr>
<tr>
<td>v12</td>
<td>657.0 (57)</td>
<td>701.7 (47)</td>
<td>706.2 (52)</td>
<td>668.5 (30)</td>
</tr>
<tr>
<td>v13</td>
<td>339.4 (10)</td>
<td>328.4 (4)</td>
<td>342.5 (6)</td>
<td></td>
</tr>
<tr>
<td>v14</td>
<td>245.8 (50)</td>
<td>250.5 (26)</td>
<td>241.5 (26)</td>
<td></td>
</tr>
<tr>
<td>v15</td>
<td>121.3 (7)</td>
<td>122.0 (3)</td>
<td>121.2 (4)</td>
<td></td>
</tr>
</tbody>
</table>

\[a\] Relative IR intensities normalized to the most intense line. Intensities of lines near 1283 cm−1 for syn-· CDCICD2; and anti-· CDCICD2 are 30.5, 58.1, and 52.6 km mol−1, respectively.

\[b\] The intensity is difficult to determine because of severe overlap with the line of C2H3Cl.
FIG. 3. (a) Difference spectrum of a Cl2/C2H2/p-H2 (1/2/6000) matrix, deposited for 7 h at 3.2 K, after irradiation at 365 nm for 5 h. (b) Difference spectra of a Cl2/C2H2/p-H2 (1/3/2000) matrix, deposited for 5 h and annealed at 4.3 K for 0.5 h, after irradiation at 365 nm for 3 h; (c) after annealing at 4.3 K for 0.5 h; (d) after further irradiation with light in the range 3870−4970 cm\(^{-1}\) with a globar for 4 h. All spectra were recorded at 3.2 K with resolution 0.25 cm\(^{-1}\). The assignments of lines in each group are A: C2H3Cl, B: CHCl2CH3, C: C2H4, C1: C2H4-HCl complex, D: C2H5Cl, E: C2H6, F: C2H5, and X: ·CHClCH3.

The assignments of lines in each group are A: C2H3Cl, B: CHCl2CH3, C: C2H4, C1: C2H4-HCl complex, D: C2H5Cl, E: C2H6, F: C2H5, and X: ·CHClCH3.

1. Assignments of observed lines in the Cl2/C2D2/p-H2 experiment

When C2H2 is replaced with C2D2, we expect that ·CDClCH2D or ·CDHCDCl to be formed if both additional hydrogen atoms come from the p-H2 matrix host. Because the 2-chloroethyl (·CH2CH2Cl) radical has been excluded as the possible carrier for lines in group X, as discussed in Sec. IV A, the most likely carrier of these features in this experiment is ·CDCICH2D. As a further proof, the predicted IR lines for conformers of ·CHDCHDCI, listed in Table S1 in the supplementary material, fail to match with our experimental observations of lines in group X.

Figure 5 compares the lines in group X observed in the Cl2/C2D2/p-H2 experiments (trace a) with the simulated IR spectra (traces c–e) for the three conformers of ·CDCICH2D. Although we are unable to exclude positively the contribution of a specific conformer, observed lines of group X in these experiments fit best with those predicted for syn-CDCICH2D, as shown in Fig. 5(c) and compared in Table IV. The line observed at 816.8 cm\(^{-1}\) with an intensity \(\sim 14\%\) of the most intense feature at 1121.4 cm\(^{-1}\) fits with one predicted at 811 cm\(^{-1}\) that has an intensity \(\sim 20\%\) of the most intense feature at 1129 cm\(^{-1}\) for syn-CDCICH2D, whereas the corresponding lines of anticlinal-CDCICH2D and anti-CDCICH2D at 822 and 807 cm\(^{-1}\) are predicted to have \(<1\%\) intensity of the most intense feature. The separation of observed lines at 1286.1 and 1246.6 cm\(^{-1}\) (39.5 cm\(^{-1}\)) also fits better with that predicted for syn-CDCICH2D (43.5 cm\(^{-1}\)) than those of anticlinal-CDCICH2D (31.2 cm\(^{-1}\)) and anti-CDCICH2D (8.8 cm\(^{-1}\)). Furthermore, the observed line at 915.2 cm\(^{-1}\) fits much better with a line predicted for syn-CDCICH2D at 929 cm\(^{-1}\) than...
TABLE V. Observed wavenumbers and relative IR intensities for lines of various groups ascribable to known species.

<table>
<thead>
<tr>
<th>Group</th>
<th>Species</th>
<th>Observed wavenumbers (cm$^{-1}$) and relative intensities$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>C$_2$HCl</td>
<td>3118.7 (2), 3088.1 (5), 1609.8 (100), 1368.1 (9), 1280.3 (15), 1029.4 (18), 943.2 (41), 896.5 (45), 717.6 (26), 712.6 (20), 619.8 (14)</td>
</tr>
<tr>
<td>B</td>
<td>CHCl$_2$CH$_3$</td>
<td>1445.8 (40), 1382.1 (26), 1232.3 (41), 1088.1 (9), 1058.7 (94), 983.1 (31), 702.8 (100), 700.9 (67), 672.5 (79), 667.7 (34)</td>
</tr>
<tr>
<td>C</td>
<td>C$_2$H$_4$</td>
<td>3097.8, 2984.5, 1440.0 (13), 948.4 (100)</td>
</tr>
<tr>
<td>C$_1$</td>
<td>C$_2$H$_4$-HCl</td>
<td>2772.6, 2770.6 (428), 1441.9 (12), 964.3 (100)</td>
</tr>
<tr>
<td>D</td>
<td>C$_2$H$_5$Cl</td>
<td>2982.9 (40), 1464.0 (32), 1455.7 (6), 1440.0 (11), 1382.7 (42), 1287.5 (87), 972.0 (100), 784.9 (14), 672.5 (79), 667.7 (34)</td>
</tr>
<tr>
<td>E</td>
<td>C$_2$H$_6$</td>
<td>2981.3 (100); 1462.9 (12); 1396.3 (7); 820.9, 822.0, 824.3 (10)</td>
</tr>
<tr>
<td>F</td>
<td>C$_2$H$_5$</td>
<td>3123.3 (?) , 3032.6 (19), 538.0 (100)</td>
</tr>
</tbody>
</table>

Cl$_2$/C$_2$H$_2$/p-H$_2$ matrix

<table>
<thead>
<tr>
<th>Group</th>
<th>Species</th>
<th>Observed wavenumbers (cm$^{-1}$) and relative intensities$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$^{13}$C$_2$H$_3$Cl</td>
<td>3073.9(6), 1561.7 (100), 1356.8 (20), 1274.9 (18), 1016.9 (38), 941.1 (66), 866.9 (59), 703.0 (34), 697.5 (24), 612.6 (17)</td>
</tr>
<tr>
<td>B</td>
<td>$^{13}$CHCl$_2$-$^{13}$CH$_3$</td>
<td>1441.3 (57), 1373.0 (27), 1222.2 (25), 1060.8 (7), 1045.5 (96), 965.3 (27), 685.2 (100), 683.4 (69), 636.8 (10), 634.7 (9)</td>
</tr>
<tr>
<td>C</td>
<td>$^{13}$C$_2$H$_4$</td>
<td>3087.9 (24), 2974.8, 1434.3 (23), 943.5 (100)</td>
</tr>
<tr>
<td>C$_1$</td>
<td>$^{13}$C$_2$H$_4$-HCl</td>
<td>2772.6, 2770.5 (424), 1435.1(15), 959.3(100)</td>
</tr>
<tr>
<td>D</td>
<td>$^{13}$C$_2$H$_5$Cl</td>
<td>2972.7, 2932.2 (17), 1461.1 (10), 1451.8 (7), 1418.1, 1372.0 (13), 1286.6 (19), 782.2 (1), 657.5 (20), 651.8 (22)</td>
</tr>
<tr>
<td>E</td>
<td>$^{13}$C$_2$H$_6$</td>
<td>2971.1 (100), 1463.0 (8), 1367.3 (1), 819.2, 820.8, 823.2 (8)</td>
</tr>
<tr>
<td>F</td>
<td>$^{13}$C$_2$H$_5$</td>
<td>3110.6?, 3026.5 (26), 534.7 (100)</td>
</tr>
</tbody>
</table>

Cl$_2$/C$_2$D$_2$/p-H$_2$ matrix

<table>
<thead>
<tr>
<th>Group</th>
<th>Species</th>
<th>Observed wavenumbers (cm$^{-1}$) and relative intensities$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_t$</td>
<td>trans-CHDCDCl</td>
<td>1560.6 (100), 1268.1 (18), 993.9 (38), 851.5 (36), 697.6 (47), 692.0 (86)</td>
</tr>
<tr>
<td>A$_c$</td>
<td>cis-CHDCDCl</td>
<td>1562.4 (100), 1032.5 (20), 867.0 (74), 821.7(8), 664.5 (33)</td>
</tr>
<tr>
<td>C</td>
<td>trans-CHDCHD</td>
<td>1295.8 (24), 986.0 (100), 724.9 (62)</td>
</tr>
<tr>
<td>C$_c$</td>
<td>cis-CHDCHD</td>
<td>1338.9 (15), 841.7 (100)</td>
</tr>
<tr>
<td>C$_H$</td>
<td>C$_2$H$_2$D</td>
<td>1398.8 (17), 942.2 (100), 805.9 (39)</td>
</tr>
<tr>
<td>C$_H^1$</td>
<td>trans-CHDCHD-HCl</td>
<td>2771.2 (188), 2769.1 (100), 996.7 (100), 743.6 (82)</td>
</tr>
<tr>
<td>D$_a$</td>
<td>syn-CH$_2$DCHDCl</td>
<td>1428.5 (64), 1329.0 (17), 1298.8 (15), 1240.6 (25), 1092.9 (100), 1011.4 (50), 926.6 (40), 792.3 (35), 626.8 (40)</td>
</tr>
<tr>
<td>D$_b$</td>
<td>anti-CH$_2$DCHDCl</td>
<td>1416.2 (62), 1322.5 (22), 1288.3 (16), 1280.9 (15), 1232.4 (37), 1091.4 (23), 992.7 (100), 675.7 (13), 660.9 (23)</td>
</tr>
</tbody>
</table>

$^a$Percentage IR intensities relative to the most intense line of the species are listed in parentheses.

those for anticlinal-CDCICH$_2$D (1005 or 871 cm$^{-1}$) and anticylindrical-CDCICH$_2$D (1038 or 848 cm$^{-1}$).

Considering the photochemical behavior and comparison of the spectral pattern of experimentally observed lines with that predicted for various isomers of isotopically substituted chloroethyl radicals, we conclude that lines in group X are due to 1-chloroethyl ($\cdot$CHClCH$_3$) radical that was not previously identified experimentally. In contrast, when Cl was added to C$_2$H$_4$, only the 2-chloroethyl ($\cdot$CH$_2$CH$_2$Cl) radical was observed.$^{29}$ In the experiments with Cl$_2$/C$_2$D$_2$/p-H$_2$,

1-chloroethyl radical $\cdot$CDCICH$_2$D is formed and the most likely configuration is syn-CDCICH$_2$D.

2. The assignment of lines in group A to trans-CHDCDCl

Lines in group A observed in the Cl$_2$/C$_2$H$_2$/p-H$_2$ experiments are due to C$_2$H$_3$Cl, as discussed in Sec. III C. In the experiment with Cl$_2$/C$_2$D$_2$/p-H$_2$, we expect that CHD-CDCl molecules are formed. This species has two stable
FIG. 4. (a) Difference spectrum of a Cl$_2$/C$_2$H$_2$/p-H$_2$ (1/1.3/4000) matrix, deposited for 8.5 h at 3.2 K, after irradiation at 365 nm for 3 h. (b) Difference spectra of a Cl$_2$/C$_2$H$_2$/p-H$_2$ (1/1/2000) matrix, deposited for 7 h at 3.2 K, after irradiation at 365 nm for 3 h; (c) after further irradiation with light in the range 3870–4970 cm$^{-1}$ from a globar lamp for 4 h. All spectra were recorded at 3.2 K with resolution 0.25 cm$^{-1}$. The assignments of lines in each group are A: $^{13}$C$_2$H$_3$Cl, B: $^{13}$CHCl$_2$, C: $^{13}$C$_2$H$_4$, C$_1$: $^{13}$C$_2$H$_4$-HCl complex, D: $^{13}$C$_2$H$_5$Cl, E: $^{13}$C$_2$H$_6$, F: $^{13}$C$_2$H$_5$, and X: $^{13}$CHCl$^{13}$CH$_3$.

isomers: trans-CHDCDCl and cis-CHDCDCl. The predicted harmonic vibrational wavenumbers of trans-CHDCDCl, cis-CHDCDCl, and CHClCD$_2$ are listed in Table S3 of the supplementary material.46

Figure 5 shows a comparison of observed lines in group A$_t$ (trace a) with calculated stick spectra for trans-CHDCDCl (trace f) and cis-CHDCDCl (trace g). The predicted spectrum of trans-CHDCDCl clearly fits better with the experimentally observed spectrum of group A$_t$ in the Cl$_2$/C$_2$D$_2$/p-H$_2$ experiment in terms of line positions and relative IR intensities. The six intense features of trans-CHDCDCl are predicted to be 1611, 1275, 997, 882, 705, and 683 cm$^{-1}$, whereas the corresponding lines of cis-CHDCDCl are predicted to be 1615, 1268, 1033, 898, and 652 cm$^{-1}$. Observed lines at 1560.6, 1268.1, 993.9, 851.5, 697.6, and 692.0 cm$^{-1}$ (trace a) fit better with those predicted for trans-CHDCDCl. The experimentally observed deuterium isotopic ratios of 0.9694, 0.9269, 0.7763, 0.9498, 0.7396, and 0.9643 for lines at 1560.6, 1268.1, 993.9, 851.5, 697.6, and 692.0 cm$^{-1}$, respectively, are in satisfactory agreement with the values 0.9683, 0.9162, 0.7734, 0.9430, 0.7326, and 0.9720 predicted with B3LYP calculations (Table S3 of the supplementary material).46

As further support, we identified lines at 1562.4, 1032.5, 867.0, 821.7 (weak), and 664.5 cm$^{-1}$ as group A$_t$ (Fig. 5(b)) upon secondary IR irradiation of the 365-nm irradiated Cl$_2$/C$_2$D$_2$/p-H$_2$ matrix. These lines might be assigned to cis-CHDCDCl according to comparison with harmonic vibrational wavenumbers and IR intensities predicted with quantum-chemical calculations. We conclude hence that lines in group A$_t$ observed in the experiments with Cl$_2$/C$_2$D$_2$/p-H$_2$ are due to trans-CHDCDCl.

C. Reaction mechanisms in $p$-H$_2$

1. Formation of C$_2$H$_3$Cl and ·CHClCH$_3$ from Cl$_2$/C$_2$H$_2$/p-H$_2$ experiments

The abstraction channel of the Cl + C$_2$H$_2$ reaction has a barrier of 123–139 kJ mol$^{-1}$, inaccessible under our experimental conditions; consequently no line ascribable to C$_2$H was observed. According to computations with the CCSD(T) or G3 method,15 the addition channel to form a C$_2$H$_2$-Cl complex, 11–17 kJ mol$^{-1}$ more stable than Cl + C$_2$H$_2$, is barrierless and the C$_2$H$_2$-Cl complex has a small barrier of $\sim$2 kJ mol$^{-1}$ for conversion to trans-CHCHCl (chlorovinyl) radicals, which are the originally expected product for the reaction of Cl + C$_2$H$_2$ in solid $p$-H$_2$ at low temperature. The energies of trans-CHCHCl are predicted to be 57–73 kJ mol$^{-1}$ smaller than Cl + C$_2$H$_2$. The barrier for isomerization of trans-CHCHCl to cis-CHCHCl is predicted to be $\sim$21 kJ mol$^{-1}$. The energy of cis-CHCHCl exceeds that of trans-CHCHCl by 4–5 kJ mol$^{-1}$.1,15

In this experiment, we observed C$_2$H$_3$Cl and ·CHClCH$_3$ as the major products but no IR absorption ascribable to trans-CHCHCl or cis-CHCHCl or the C$_2$H$_2$-Cl complex.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP:
These results indicate that the originally expected primary products, \( \text{trans-CHCHCl} \) and/or \( \text{cis-CHCHCl} \), might react readily with a neighboring \( \text{p-H}_2 \) molecule to form \( \text{C}_2\text{H}_3\text{Cl} \) and \( \cdot\text{CHClCH}_3 \). This assumption is supported by the results of experiments with the \( \text{Cl}_2/\text{C}_2\text{D}_2/\text{p-H}_2 \) matrix, in which \( \text{trans-CHDCDCl} \) and \( \cdot\text{CDClCH}_2\text{D} \) were formed, indicating that the extra H atoms come from the matrix host, not from the reactant \( \text{C}_2\text{D}_2 \). The most likely processes for the reaction of \( \cdot\text{CHCHCl} \) are thus

\[
\text{CHCHCl} + \text{H} \rightarrow \text{C}_2\text{H}_3\text{Cl} + \text{H} \tag{1}
\]

\[
\text{C}_2\text{H}_3\text{Cl} + \text{H} \rightarrow \cdot\text{CHClCH}_3 \text{(1-chloroethyl)} \tag{2a}
\]

\[
\rightarrow \cdot\text{CH}_2\text{CH}_2\text{Cl} \text{(2-chloroethyl).} \tag{2b}
\]

The H atom produced in reaction (1) might also react with CHCHCl to form \( \text{C}_2\text{H}_3\text{Cl} \),

\[
\cdot\text{CHCHCl} + \text{H} \rightarrow \text{C}_2\text{H}_3\text{Cl}. \tag{3}
\]

The enthalpy change of reaction (1) is about \(-6 \text{ kJ mol}^{-1}\) if we compare the bond energy of \( \text{H}_2 \) (436 kJ mol\(^{-1}\)) and the enthalpy change of \(-442 \text{ kJ mol}^{-1}\) for reaction (3) predicted with the QCISD(T)/6-311+G(d,p) method.\(^{59}\)

Mebel \textit{et al.} investigated a similar system \( \text{C}_2\text{H}_3 + \text{H}_2 \) using UMP2/6-311G(d,p) and QCISD/6-311G(d,p) methods and concluded that direct 1,1- or 1,2-insertion of \( \text{H}_2 \) to \( \text{C}_2\text{H}_3 \) to form \( \text{C}_2\text{H}_5 \) does not occur. The reaction proceeds with a barrier of height 44 kJ mol\(^{-1}\) to form \( \text{C}_2\text{H}_4 + \text{H} \), followed by a second barrier of height 20 kJ mol\(^{-1}\) to form \( \text{C}_2\text{H}_5 \), which has energy 169 kJ mol\(^{-1}\) smaller than that of \( \text{C}_2\text{H}_3 + \text{H}_2 \).\(^{60}\) The reaction channels of the reaction \( \text{C}_2\text{H}_3 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_3 \) are similar to those of reactions (1) and (2).

We performed similar calculations on the \( \cdot\text{CHCHCl} + \text{H}_2 \) system using the G2//MP2/6-311++G(d,p) method and found a similar trend, as shown in Fig. 6. Reaction (1) proceeds with a barrier of height 32 kJ mol\(^{-1}\) to form \( \text{C}_2\text{H}_3\text{Cl} + \text{H} \). Reaction (2a) is followed by a second barrier of height 10 kJ mol\(^{-1}\) to form \( \cdot\text{CHClCH}_3 \), which has energy 194 kJ mol\(^{-1}\) lower than that of \( \cdot\text{CHCHCl} + \text{H}_2 \). Reaction (2b) has a barrier of height 24 kJ mol\(^{-1}\) to form \( \cdot\text{CH}_2\text{CH}_2\text{Cl} \), which has energy 177 kJ mol\(^{-1}\) lower than that of \( \cdot\text{CHCHCl} + \text{H}_2 \). According to calculations using the QCISD(T)/aug-cc-pVDZ method, the energy of 1-chloroethyl is \(-10 \text{ kJ mol}^{-1}\) less than that of 2-chloroethyl,\(^{45}\) our calculated value of 17 kJ mol\(^{-1}\) is consistent with this result. Reaction (2) was also investigated by Barat and Bozzelli using the quantum Rice-Ramsperger-Kassel (QRKK) method. An activation energy of 12 kJ mol\(^{-1}\) and exothermicity of 169 kJ mol\(^{-1}\) were derived for reaction (2a), whereas an activation energy of 24 kJ mol\(^{-1}\) and exothermicity of 152 kJ mol\(^{-1}\)
were derived for reaction (2b). Our calculated barriers agree with their values.

Although reaction (1) has a barrier of height 32 kJ mol\(^{-1}\), similar to that of C\(_2\)H\(_3\) + H\(_2\), the exothermicity of the reaction,

\[
\text{Cl} + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl},
\]

predicted to be \(\sim70\) kJ mol\(^{-1}\), is much larger than the barrier of reaction (1). Reaction (1) might hence proceed through the transition state to form C\(_2\)H\(_2\)Cl and H, and subsequently \(\cdot\)CHCICH\(_3\). For this reason, we observed C\(_2\)H\(_2\)Cl and \(\cdot\)CHCICH\(_3\) as the major products upon irradiation of the Cl\(_2\)/C\(_2\)H\(_2\)/p-H\(_2\) matrix at 365 nm.

In these experiments, only \(\cdot\)CHCICH\(_3\) (1-chloroethyl), not \(\cdot\)CH\(_2\)CH\(_2\)Cl (2-chloroethyl) radical, was observed as a major product. The reason might be that the H atom produced in reaction (1) is near the C atom attacked by the first H atom, rather than the C atom bound to the Cl atom. Reaction (2a) is hence much more facile than reaction (2b). That the activation energy predicted for reaction (2b) is much larger than that for reaction (2a) might also play an important role. The barrier height for the interconversion between 1- and 2-chloroethyl radicals is about 167 kJ mol\(^{-1}\), too large to overcome under our experimental conditions.

2. Formation of trans-CHDCDCl and \(\cdot\)CDCICH\(_2\)D from the Cl\(_2\)/C\(_2\)D\(_2\)/p-H\(_2\) experiments

According to a similar mechanism, for reactions involving Cl + C\(_2\)D\(_2\), we expect to observe CHDCDCl from reaction (5) and \(\cdot\)CDCICH\(_2\)D from reaction (6a)

\[
\cdot\text{CDCDCl} + \text{H}_2 \rightarrow \text{CHDCDCl} + \text{H},
\]

CHDCDCl + H \(\rightarrow\) CDCICH\(_2\)D (1-chloroethyl) \(\rightarrow\) CHDCDCl (2-chloroethyl),

consistent with our observation. The observation of only trans-CHDCDCl, not cis-CHDCDCl, might indicate that trans-CD CDCCl is formed initially but it is so reactive that it reacts with H\(_2\) before it has a chance to isomerize to cis-CD CDCCl. Production of syn-CD CDCICH\(_2\)D, the conformer with the lowest energy, is consistent with the expectation that internal rotation around the C–C bond has a small barrier in solid p-H\(_2\).

3. Product formation upon secondary IR irradiation

Upon secondary IR irradiation, the H\(_2\) molecule is excited and can react with Cl atoms or other free radicals produced after the 365-nm irradiation of the Cl\(_2\)/C\(_2\)H\(_2\)/p-H\(_2\) matrix. The reaction of Cl with excited H\(_2\) produces H atoms and HCl. The H atoms thus produced might react subsequently with other species in the matrix, leading to various products.

In this IR-irradiation experimental step we observed the formation of C\(_2\)H\(_2\)Cl, C\(_2\)H\(_4\), and C\(_2\)H\(_6\)Cl as major products, and C\(_2\)H\(_4\) and C\(_2\)H\(_6\) as minor products. The formation of additional amount of C\(_2\)H\(_2\)Cl might be a result of the reaction of H with C\(_2\)H\(_2\) to form C\(_2\)H\(_3\), which subsequently reacts with a nearby Cl atom to form C\(_2\)H\(_2\)Cl. Similarly, C\(_2\)H\(_3\) might react with H\(_2\) to form C\(_2\)H\(_4\) and C\(_2\)H\(_6\), which might react with another H atom to form C\(_2\)H\(_6\). The formation of C\(_2\)H\(_2\)Cl is most likely a result of reaction between \(\cdot\)CHCICH\(_3\) and H or activated H\(_2\).

In the Cl\(_2\)/C\(_2\)D\(_2\)/p-H\(_2\) experiments, the formation of trans-CHDCHD, cis-CD CICH\(_3\), and syn- and anti-CHDCHICH\(_2\)D as major products corresponds to products C\(_2\)H\(_2\), C\(_2\)H\(_2\)Cl, and C\(_2\)H\(_2\)Cl\(_2\), respectively, from the Cl\(_2\)/C\(_2\)H\(_2\)/p-H\(_2\) experiments; cis-CHDCHD and trans-CD CICH\(_2\)D were observed as minor products. The presence of both cis and trans conformers indicates that the IR light might induce the interconversion between these two conformers.

V. CONCLUSION

Upon irradiation of matrix samples of Cl\(_2\)/C\(_2\)H\(_2\)/p-H\(_2\) at 3.2 K with light at 365 nm, we observed C\(_2\)H\(_2\)Cl and the \(\cdot\)CHCICH\(_3\) (1-chloroethyl) radical as two major products. The originally expected products of the Cl + C\(_2\)H\(_2\) addition reaction, the chlorovinyl (\(\cdot\)CHCHCl) radicals, were unobserved. The assignments of lines at 2861.2, 1442.6, 1426.6, 1377.1, 1283.4, 1027.6, and 738.2 cm\(^{-1}\) to \(\cdot\)CHCICH\(_3\) are based on a consideration of possible reactions and a comparison of observed and quantum-chemically predicted vibrational wavenumbers, relative IR intensities, and their isotopic shifts when \(^{13}\)C\(_2\)H\(_2\) and C\(_2\)D\(_2\) replaced C\(_2\)H\(_2\).
when matrix samples of Cl$_2$/C$_2$D$_2$/p-H$_2$ were irradiated at 365 nm.

When the 365-nm irradiated mixtures of Cl$_2$/C$_2$H$_2$/p-H$_2$ were subsequently irradiated with IR light, which excited H$_2$ in the matrix and induced its reaction with Cl to form HCl and H atoms, C$_2$H$_3$Cl, C$_2$H$_4$, and C$_2$H$_5$Cl were observed as major products. Observation of trans-CHDCHD, cis-CDICICH$_2$, and syn- and anti-CHDCICH$_2$D as major products in the IR irradiated matrix samples of Cl$_2$/C$_2$D$_2$/p-H$_2$ further support the proposed mechanism.

Although this work demonstrates one disadvantage of using p-H$_2$ as a matrix host for spectroscopy of free radicals, as the host might react with highly reactive free radicals even at low temperature, the latter reaction might produce other free radicals—in this experiment, the 1-chloroethyl radical, ·CHCICH$_3$—that are difficult to produce using conventional methods.

ACKNOWLEDGMENTS

National Science Council of Taiwan (Grant No. NSC99-2745-M009-001-ASP) and Taiwan Ministry of Education (“Aim for the Top University Plan” of National Chiao Tung University) supported this work. The National Center for High-Performance Computing provided computer time.