An Ab Initio Study of the Potential Energy Surface of the Reaction $CHCl^{2+} + H_2$ and Comparison with Experimental Data

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Reaction pathways that lead to products of the reactions in the $[CHCl]^{2+} + D_2$ system ($CHCl^+$, CCl^+, $CHDCl^+$, HD_2^+, D_2^+, as observed experimentally) were studied using the CCSD(T)/cc-pVTZ method. Energies of located stationary points on the potential energy hypersurface were refined by the G2 method. Both isomers of the reactant dication $CHCl^{2+}$—$HCCl^{2+}$ (with H atoms bonded to C atoms) and $CClH^{2+}$ (with H atoms bonded to Cl atoms)—were taken into consideration. The calculated reaction pathways were of importance in the interpretation of experimental beam-scattering data. The heats of formation of the reactant dications $HCCl^{2+}$ and $CClH^{2+}$ and of all relevant products ions (CCl^+, $HCCl^+$, $CClH^+$, H_2CCl^+, $HCClH^+$) were calculated.

1. Introduction

The chemical reactivity of small molecular dications and their unusual features recently have been attracting an increasing amount of attention from chemists. The unusual features of the chemical reactivity of dications include high energy content of the reactants, high exoergicity of chemical reactions, the formation of electronically excited products, frequent further dissociation of primary reaction products, and the formation of a pair of singly charged products and Coulomb repulsion between them, leading to high translational energy of products, the formation of fast "naked" protons in reactions with hydrogen, impulsive proton-transfer reactions of hydrogen-containing molecular dications, etc. Most molecular dications are metastable, with respect to decomposition to two thermodynamically more stable singly charged ions. The ionization energies of molecular cations to form dications are usually 15−30 eV, and the dications easily react in charge transfer and dissociative charge-transfer processes.

Bond-forming reactions of molecular dications[1] have been observed in an increasing number of systems. They occur typically in competition with charge-transfer processes that often dominate among the reaction products. Dissociative processes, both for charge transfer and chemical reactions, are rather frequent. More-detailed studies have been conducted on systems such as $CF_2^{2+} + D_2$,[2,3] HD,[4,5] $CO_2^{2+} + D_2$,[6] HD,[7] and $CF_3^{2+} + HD$.[7,8] The $CHCl^{2+}$ dication represents a rather different system than CF_2^{2+}, CF_3^{2+}, or CO_2^{2+}. The presence of a H atom suggests a strong acidic nature,[9] which should affect its reactivity.

A motivation for this study comes from the investigation of the dynamics of chemical reactions and charge-transfer processes in collisions of the molecular dication $CHCl^{2+}$ with deuterium[10] and noble gases[11] in crossed-beam scattering experiments. In the reaction with D_2, three main products were identified, namely $CHCl^+$, CCl^+, and $CHDCl^+$.[10] Contour diagrams of the ion products, relative differential cross sections, and relative translational-energy distribution of the products were obtained from the scattering experiments, and conclusions on the dynamics of the processes could be made. The product ion $CHCl^+$ was shown to originate from a nondissociative charge-transfer process of the ground and excited states of two isomers of the reactant dication, namely $HCCl^{2+}$ and $CClH^{2+}$ (i.e., with the H atom being bonded either to the C atom or to the Cl atom). An experimental[11] and theoretical[12] study of charge transfer with noble gases helped to identify the respective state-to-state processes. The chemical reaction products were $CHDCl^+ + D^+$, formed in processes that involved the formation of reaction intermediates of two different mean lifetimes, presumably in reactions of both molecular dication isomers. Finally, CCl^+ was shown to be formed mainly in an impulsive chemical reaction of proton transfer (the other product was HD_2^+) from the reactant $HCCl^{2+}$ in the ground state; a portion of this product was formed in further dissociation of the chemical reaction product $CHDCl^+$. The proton-transfer reaction was confirmed by measuring integral cross sections of the reactions with D_2[11,13] and identification of both reaction products of the proton-transfer process. Similar results were obtained for the reaction of $CHCl^{2+}$ with argon (which resulted in the formation of $CCl^+ + ArH^+$).[13]

Considerable attention has been given to the dication $CHCl^{2+}$. An experimental study[14] identified the dication $CHCl^{2+}$ as a long-lived fragment of CH_3Cl^{2+}. In a theoretical study,[15] dissociation channels of the dication CH_3Cl^{2+} were studied and partial information on the potential energy surface was obtained. A complete active space-self-consistent field calculation, together with the TZP basis set (CASSCF/TZP), was used in this study. However, the authors referred to the H−C−Cl^{2+} isomer only. This work, as well as several others,[10,16,17] pointed out the important rearrangement of the chloromethane dication, which leads to the dication of its ylide form, CH_2ClH^{2+}.

The aim of the present study is to calculate the potential energy hypersurface (PES) of the $CHCl^{2+} + H_2$ system at a uniform and reliable level of theory and to provide sufficiently accurate data for the interpretation of previous experimental results of crossed-beam studies of charge transfer and chemical reactions in this system.

2. Computational Method

The calculations were performed using the coupled cluster method CCSD(T),[18−21] in conjunction with Dunning's correla-

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tion consistent triple-ζ basis set (cc-pVTZ),[22−24] as implemented in the Gaussian 98 method.[25] For all the optimized structures, frequency analysis at the same level of theory was used to assign them as real minima and transitions structures on the PES. Energies of all the stationary points were refined by the G2 method.[26] The G2 energies were calculated for the CCSD(T) optimized structures and include the CCSD(T) zero-point vibrational energy. All the structures were pre-optimized at the density functional theory level, using the same basis set (B3LYP/cc-pVTZ). The basis set superposition error was calculated for the loosely bound complexes (see Section 3.3.1 presented later in this paper) and was observed to be practically negligible (<0.01 eV).

3. Results and Discussion

For the reactant $CHCl^{2+}$, two possible stable isomers—$HCCl^{2+}$ and $CClH^{2+}$, with H atoms bonded either to C or to Cl atom, respectively—were taken into consideration. The basic aim of this study was to construct the singlet PES that corresponds to the ground states of both isomers. In addition, several structures were optimized in the triplet electronic states to complete the overall picture (these structures are denoted with an asterisk (*)). All optimized structures, i.e., the minima and the transition states, are shown in Figure 1. The CCSD(T) total energies (ϵ_0), the zero-point energy (ZPE) corrections (ϵ_{ZPE}), and G2 energies (E_0) are given (in hartrees) in Table 1. Table 2 lists the relative energies $(\Delta\epsilon_0)_{rel}$, $(\Delta(\epsilon_0 + \epsilon_{ZPE}))_{rel}$, and $(\Delta E_0)_{rel}$ of the individual points on the reaction hypersurface. The relative values are related to the energy of $HCCl^{2+} + H_2$ and have been recalculated in terms of electron volts. Minima on the PES (all frequencies are real) are denoted as **Mx** (**x** indicates a number), whereas the transition structures (those which possess one imaginary frequency) are denoted as **TSx** (**x** is a number).

The dication $HCCl^{2+}$ (**M1**) has a linear structure with a very short C−Cl bond (1.48 Å), because it is an efficient overlap of the C and Cl bonding orbitals, which leads formally to a triple bond between these both partners. The first excited triplet state (**M1***) lies 4.23 eV above it and has a bent geometry. The other isomer, $C-Cl-H^{2+}$ (**M3**), is higher in energy than $H-C-Cl^{2+}$(**M1**), by 3.02 eV. In the isomer M3, the C−Cl bond is a single bond and, thus, is correspondingly longer (1.74 Å). The two lone pairs of electrons located on Cl atom lead to a bent geometry, with a bonding angle of 94.4°. The isomerization of these two dications ($HCCl^{2+} \leftrightarrow CClH^{2+}$) proceeds via the transition state **TS1**. The barrier height calculated for this isomerization ($HCCl^{2+} \rightarrow CClH^{2+}$) is 3.83 eV. For the reverse process ($CClH^{2+} \rightarrow HCCl^{2+}$), the calculation gives a barrier height of 0.81 eV. The first triplet excited state of the dication $CClH^{2+}$ (**M3***) lies 2.08 eV above the ground state. The detailed computational study of the ground state and the low-lying excited states of both dication isomers, $HCCl^{2+}$ and $CClH^{2+}$, has been published separately.[12] The method applied was the averaged quadratic coupled cluster method (AQCC), using complete active reference space and a moderate atomic natural orbital basis set. This method is regarded as quite accurate for calculations of excited states and can be viewed as a multi-reference approach to the coupled cluster method, as presented here. The results for the single reference AQCC converge to the CCSD, as demonstrated by small differences of ∼0.02 eV between the energies calculated with the use of the CCSD(T) and AQCC methods. The excitation energies from the singlet ground state to the first excited triplet state, obtained with the AQCC−CASSCF method, were 4.13 eV for $HCCl^{2+}$ (CCSD(T) calculations gave a value of 4.12 eV) and 1.94 eV for $CClH^{2+}$

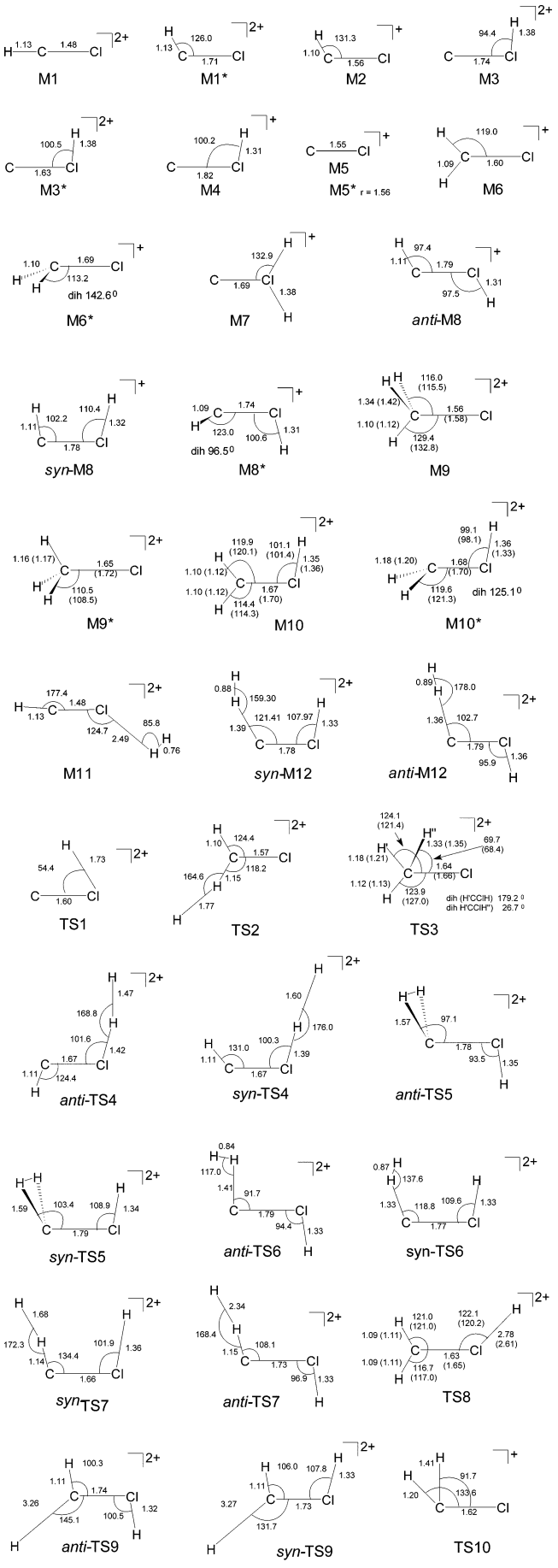


Figure 1. CCSD(T) optimized structures of minima and transition states on the potential energy surface of the $CHCl^{2+} + H_2$ reaction.

TABLE 1: CCSD(T)/cc-pVTZ Total Energies (ϵ_0), ZPE Corrections (ϵ_{ZPE}), and G2//CCSD(T)/cc-pVTZ Total Energies (E_0) for Optimized Stationary Point[a]

	CCSD(T)/cc-pVTZ			G2//CCSD(T)/cc-pVTZ
ion	total energy, ϵ_0 (hartree)	zero-point energy correction, ϵ_{ZPE} (hartree)	number of imaginary frequencies, N_{imag}	E_0 (hartree)
$HCCl^{2+}$				
(**M1**)	−497.2561284	0.013103	0	−497.2624212
(**M1***)	−497.1046050	0.010099	0	−497.1068969
$HCCl^+$ (**M2**)	−497.8949245	0.011787	0	−497.9013499
$CClH^{2+}$				
(**M3**)	−497.1433105	0.008100	0	−497.1513534
(**M3***)	−497.071144	0.009020	0	−497.0750002
$CClH^+$ (**M4**)	−497.8039271	0.009000	0	−498.4060908
CCl^+				
(**M5**)	−497.2783858	0.002664	0	−497.2938751
(**M5***)	−497.1615560	0.002505	0	−497.1731195
H_2CCl^+				
(**M6**)	−498.5824924	0.025311	0	−498.5784022
(**M6***)	−498.4675510	0.021189	0	−498.4615406
$CClH_2^+$ (**M7**)	−498.2858216	0.014765	0	−498.2963570
$HCClH^+$				
anti-$HCClH^+$ (*anti*-**M8**)	−498.4586091	0.020779	0	−498.4571974
syn-$HCClH^+$ (*syn*-**M8**)	−498.4541564	0.020206	0	−498.4538246
(**M8***)	−498.4430840	0.020018	0	−498.4377691
H_2HCCl^{2+}				
(**M9**)	−498.4704983	0.029096	0	−498.4623216
(**M9***)	−499.0377061	0.027862	0	−498.4066984
H_2CClH^{2+}				
(**M10**)	−498.5375510	0.033183	0	−498.5242254
(**M10***)	−498.4003345	0.025417	0	−498.3905748
$HCCl-H_2^{2+}$ (**M11**)	−498.4378949	0.024936	0	−498.4367444
H_2-CClH^{2+}				
anti-H_2-CClH^{2+} (*anti*-**M12**)	*−498.3714302*	*0.022655*	*0*	*−498.3687874*
syn-H_2-CClH^{2+} (*syn*-**M12**)	*−498.3627802*	*0.022655*	*0*	*−498.3597843*
TS1	−497.1096583	0.005105	1	−497.1217543
TS2	−498.4300125	0.023837	1	−498.4292027
TS3	−498.4450876	0.026906	1	−498.4381582
anti-**TS4**	−498.3622779	0.019380	1	−498.3578750
syn-**TS4**	−498.3569943	0.019581	1	−498.3497755
anti-**TS5**	−498.3733350	0.022866	1	−498.3694716
syn-**TS5**	−498.3637989	0.021975	1	−498.3613415
anti-**TS6**	*−498.3698752*	*0.022592*	*1*	*−498.3666267*
syn-**TS6**	*−498.3646262*	*0.021608*	*1*	*−498.3636525*
anti-**TS6′**	−498.3694698	0.020676	2	−498.3683203
anti-**TS7**	−498.3306316	0.019317	1	−498.3350259
syn-**TS7**	−498.3411639	0.019938	1	−498.3408807
TS8	−498.4507740	0.026015	1	−498.4471218
anti-**TS9**	−498.3572883	0.022264	1	−498.3555224
syn-**TS9**	−498.3565486	0.021758	1	−498.3552494
TS10	−498.4238672	0.015934	1	−498.4293405

[a] Values given in italics denote that the corresponding energy was calculated for the CCSD(T)/6-31++G** optimized structure.

(CCSD(T) gave a value of 1.96 eV). The ionization energies obtained from the AQCC calculations for $HCCl^+$ and $CClH^+$ were 17.31 and 17.92 eV, respectively. The CCSD(T) ionization energies of the two isomeric cations were 17.38 and 17.98 eV, respectively.

To complement the information, we list here also the CCSD(T) calculated harmonic frequencies of both dication isomers. They are as follows: 2822.1 (σ_g), 1343.2 (σ_g), and 793.1(π) cm^{-1} for $HCCl^{2+}$ and 2148.9 (a′), 752.4 (a′), and 654.1 (a′) cm^{-1} for $CClH^{2+}$.

3.1. Charge Transfer: Formation of $CHCl^+$. Charge transfer is usually the dominant process in reactions of dications with neutrals.[1−7] However, in the case of the reaction of $CHCl^{2+}$ with D_2 (the same is true for H_2), the situation is different. According to the experimental results,[10] the nondissociative charge-transfer reaction is only a minor process. The explanation seems to follow from the reaction window concept.[27] This concept predicts that charge transfer has a large cross section only if the reaction exoergicity is ∼2−5 eV. Based on our calculations, the exoergicities of the charge-transfer processes of the ground states of $HCCl^{2+}$ and $CClH^{2+}$ with H_2 are only 1.90 and 2.42 eV, respectively.

$$HCCl^{2+}\,(\mathbf{M1}) + H_2 \rightarrow HCCl^{+}\,(\mathbf{M2}) + H_2^{+} \quad (\Delta E = 1.90\ \text{eV}) \quad (1)$$

$$CClH^{2+}\,(\mathbf{M3}) + H_2 \rightarrow CClH^{+}\,(\mathbf{M4}) + H_2^{+} \quad (\Delta E = 2.42\ \text{eV}) \quad (2)$$

The exoergicity ΔE is defined as a difference of G2 electronic energy of reactants and products, including the ZPE (see the E_0 values in Tables 1 and 2). Results of experimental studies of the $CHCl^{2+}$ reaction with argon (which has an ionization energy, 15.75 eV, that is similar to that with H_2, 15.43 eV) implied that both ground and excited states of $CHCl^{2+}$ were involved in the charge-transfer process.[11] A comparison of the experimental data with the AQCC calculations[12] led to the conclusion that the states that contributed to the formation of

TABLE 2: Relative Energies (Related to the Total Energy of Reactants $HCCl^{2+} + H_2$) of Calculated Points on the Hypersurface of the Reaction $HCCl^{2+} + H_2$[a]

	CCSD(T)/cc-pVTZ		G2
	$\Delta(\epsilon_0)_{rel}$	$\Delta(\epsilon + \epsilon_{ZPE})_{rel}$	$\Delta(E_0)_{rel}$
$HCCl^{2+}$			
(**M1**) + H_2	0	0	0
(**M1***) + H_2	4.12	4.04	4.23
$HCCl^+$ (**M2**) + H_2^+	−1.87	−2.03	−1.90
$CClH^{2+}$			
(**M3**) + H_2	3.07	2.93	3.02
(**M3***) + H_2	5.03	4.65	5.10
$CClH^+$ (**M4**) + H_2^+	0.61	0.37	0.60
CCl^+			
(**M5**) + H_3^+	−5.21	−5.21	−5.30
(**M5***) + H_3^+	−2.03	−2.04	−2.02
(**M5**) + H_2 + H^+	−0.61	−0.89	−0.86
(**M5***) + H_2 + H^+	2.57	2.29	2.43
H_2CCl^+			
(**M6**) + H^+	−4.19	−4.13	−4.09
(**M6***) + H^+	−1.06	−1.12	−0.91
$CClH_2^+$ (**M7**) + H^+	3.88	3.65	3.59
$HCClH^+$			
anti-$HCClH^+$ (*anti*-**M8**) + H^+	−0.82	−0.88	−0.79
syn-$HCClH^+$ (*syn*-**M8**) + H^+	−0.70	−0.78	−0.70
(**M8***) + H^+	−0.40	−0.48	−0.26
H_2HCCl^{2+} (**M9**)	−1.14	−0.98	−0.93
H_3CCl^{2+} (**M9***)	−0.17	−0.04	0.17
H_2CClH^{2+}			
(**M10**)	−2.97	−2.70	−2.61
(**M10***)	0.77	0.83	1.02
$HCCl-H_2^{2+}$ (**M11**)	−0.26	−0.21	−0.23
H_2-CClH^{2+}			
anti-H_2-CClH^{2+} (*anti*-**M12**)	*1.55*	*1.54*	*1.62*
syn-H_2-CClH^{2+} (*syn*-**M12**)	*1.79*	*1.77*	*1.86*
TS1+ H_2	3.99	3.77	3.83
TS2	−0.04	−0.02	−0.03
TS3	−0.45	−0.35	−0.27
anti-**TS4**	1.80	1.70	1.91
syn-**TS4**	1.94	1.85	2.13
anti-**TS5**	1.50	1.49	1.60
syn-**TS5**	1.76	1.73	1.82
anti-**TS6**	*1.59*	*1.58*	*1.68*
syn-**TS6**	*1.74*	*1.70*	*1.76*
anti-**TS6′**	1.61	1.54	1.63
anti-**TS7**	2.66	2.56	2.54
syn-**TS7**	2.38	2.29	2.38
TS8	−0.61	−0.53	−0.52
anti-**TS9**	1.94	1.91	1.98
syn-**TS9**	1.96	1.92	1.98
TS10	0.13	−0.07	−0.03

[a] All values given in units of eV. Values given in italics denote that the corresponding energy was calculated for the CCSD(T)/6-31++G** optimized structure.

the charge-transfer products were the ground state of the isomer $HCCl^{2+}$ (reaction), the ground state of the other isomer $CClH^{2+}$ (reaction), and also the first excited triplet state of $CClH^{2+}$. This excited state is located 2.08 eV (AQCC calculation gave a value of 1.94 eV) above the ground state of $CClH^{2+}$, and, thus, the exoergicity of the charge-transfer process with H_2 is 4.50 eV, matching the reaction window very well.[27] Therefore, it was assumed that this state preferentially reacted via charge transfer and was not significantly involved in chemical reactions.

Figure 2a shows the relative translational-energy distribution $P(T')$ of the charge-transfer products $CHCl^+ + D_2^+$ plotted against the reaction exoergicity $\Delta E = T' - T$, as obtained from the experiments.[10] Charge-transfer channels of the ground and the first electronic excited state of the isomer $CClH^{2+}$ (exoergicities marked with solid arrows in Figure 2a) explain the bulk of the broad peak of the $P(T')$ curve. The ground state of the dication reactant $HCCl^{2+}$ contributes to the charge-transfer

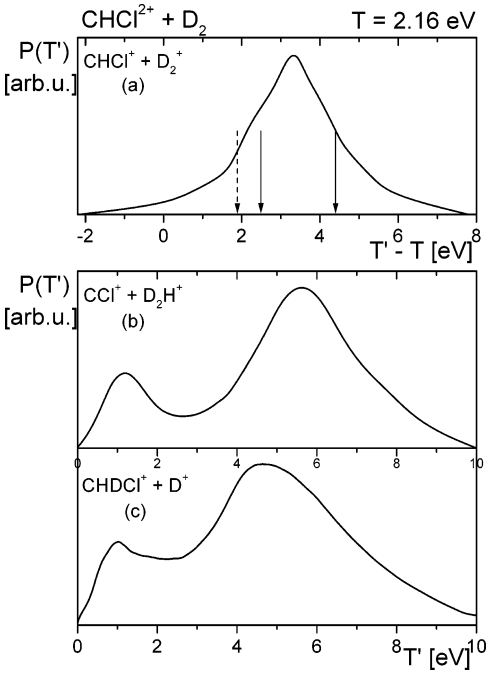


Figure 2. Relative translational-energy distributions, $P(T')$, of products (a) $CHCl^+ + D_2^+$, (b) $CCl^+ + D_2H^+$, and (c) $CHDCl^+ + D^+$ from collisions of $CHCl^{2+} + D_2$ ($T = 2.16$ eV) plotted against the reaction exoergicity $\Delta E = T' - T$ (panel a) or product-relative translational energy T′ (panels b and c).

channels only marginally (dashed arrow in Figure 2a). For a more detailed discussion of the charge-transfer results and the role of excited states of $CHCl^{2+}$ in this reaction, see the companion paper in this issue.[10]

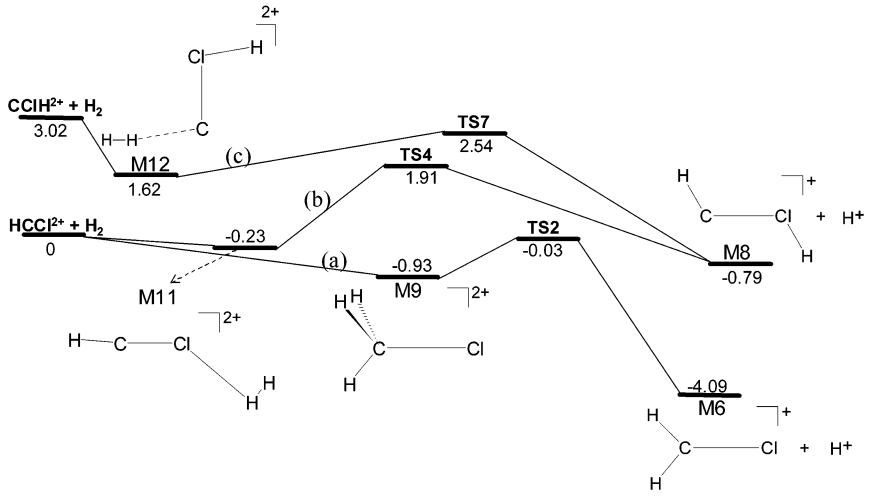
3.2. Formation of CCl^+ (M5). The major process in the reaction of $CHCl^{2+}$ with D_2 (the same holds for H_2) is the formation of CCl^+. The product ion CCl^+ originates mainly in proton transfer from the dication $CHCl^{2+}$ to molecular H_2, which is characterized by a rather high exoergicity. Both isomers of the dication can react:

$$HCCl^{2+}\ (\mathbf{M1}) + H_2 \rightarrow CCl^+\ (\mathbf{M5}) + H_3^+ \quad (\Delta E = 5.30\ \text{eV}) \quad (3)$$

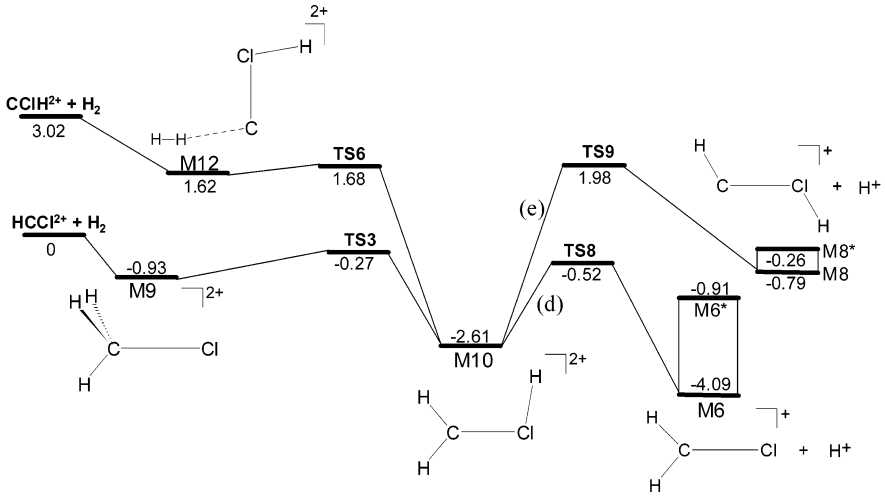
$$CClH^{2+}\ (\mathbf{M3}) + H_2 \rightarrow CCl^+\ (\mathbf{M5}) + H_3^+ \quad (\Delta E = 8.32\ \text{eV}) \quad (4)$$

All attempts to localize a transition state for the proton transfer from either $HCCl^{2+}$ or $CClH^{2+}$ to the molecule H_2 were unsuccessful. The optimization of the corresponding structures led to a stationary point of a higher order or led to dissociation into CCl^+ and H_3^+. This finding, which implies no intermediate in this reaction, is in agreement with the conclusion from the experimental results,[10] namely that the proton-transfer reaction is a direct process, which is characterized by a strong forward scattering of the product CCl^+. The relative translational-energy distribution of the products $CCl^+ + HD_2^+$, $P(T')$ vs T', is shown in Figure 2b. The proton transfer to D_2 causes the broad peak that is located in the range of 3−10 eV in the $P(T')$ curve (the collision energy T was 2.16 eV). The smaller peak, at ∼1.2 eV, results from a further decomposition of the charge-transfer product $CHDCl^+$ and will be discussed in Section 3.4. The calculated exoergicities suggest that the dication reactant in the proton-transfer reaction is mainly the ground state of the isomer $HCCl^{2+}$ (**M1**; see reaction 3), with a less significant contribution from $CClH^{2+}$ (**M3**, see reaction 4).

SCHEME 1. Pathways to [CH_2Cl^+] via "Loosely Bound" Complexes



SCHEME 2. Pathways to [CH_2Cl^+] via "Stable" Intermediate M10



The triplet excited state of CCl^+ (**M5***) lies 3.29 eV above the ground state **M5** (the AQCC excitation energy is 3.16 eV).

3.3. Formation of H_2CCl^+ (M6) and $HCClH^+$ (M8) in Chemical Reactions. The calculated exoergicities of the possible processes between reactant dication isomers and product ion isomers are as follows:

$$HCCl^{2+}\ (\mathbf{M1}) + H_2 \rightarrow H_2CCl^+\ (\mathbf{M6}) + H^+ \qquad (\Delta E = 4.09\ \text{eV}) \quad (5)$$

$$CClH^{2+}\ (\mathbf{M3}) + H_2 \rightarrow H_2CCl^+\ (\mathbf{M6}) + H^+ \qquad (\Delta E = 7.11\ \text{eV}) \quad (5')$$

$$HCCl^{2+}\ (\mathbf{M1}) + H_2 \rightarrow CClH_2^+\ (\mathbf{M7}) + H^+ \qquad (\Delta E = -3.59\ \text{eV}) \quad (6)$$

$$CClH^{2+}\ (\mathbf{M3}) + H_2 \rightarrow CClH_2^+\ (\mathbf{M7}) + H^+ \qquad (\Delta E = -0.57\ \text{eV}) \quad (6')$$

$$HCCl^{2+}\ (\mathbf{M1}) + H_2 \rightarrow HCClH^+\ (\mathbf{M8}) + H^+ \qquad (\Delta E = 0.79\ \text{eV}) \quad (7)$$

$$CClH^{2+}\ (\mathbf{M3}) + H_2 \rightarrow HCClH^+\ (\mathbf{M8}) + H^+ \qquad (\Delta E = 3.81\ \text{eV}) \quad (7')$$

Three stable isomers are considered for the product of the chemical reaction between the dications $HCCl^{2+}$ (**M1**) and $CClH^{2+}$ (**M3**) (see Figure 1a). The isomer H_2CCl^+ (**M6**) has both H atoms attached to the C atom, $CClH_2^+$ (**M7**) has both H atoms bonded to the Cl atom, and finally $HCClH^+$ (**M8**) has one H atom attached to the C atom and the other one to the Cl atom. In addition, this H−C−Cl−H$^+$ isomer can exist in two rotamers: either as *anti*-**M8**, with the anti-periplanar arrangement of the H atoms (torsion angle of 180°), or as *syn*-**M8**, with syn-periplanar arrangement of the two H atoms (torsion angle of 0°). A rotational barrier of a considerable height (0.64 eV) was observed for the transition from *anti*-**M8** to *syn*-**M8.** The anti-periplanar arrangement is more stable than the syn-periplanar arrangement, by 0.09 eV.

All energies given in Schemes 1 and 2 refer to the more-stable anti-isomers. Energies of the corresponding syn-structures can be found in Tables 1 and 2 and in the following text. In addition to the singlet states, triplet states of H_2CCl^+ and $HCClH^+$ were also optimized. They are denoted by an asterisk (*) in Tables 1 and 2 and in Figure 1a. Optimization of the structure of the cation $CClH_2^+$ in the triplet state led to its dissociation along the C−Cl bond.

The calculated reaction pathways have a common feature. The first step is the formation of a "loosely bound" complex between the original dication and H_2, with the charge being delocalized over the entire complex. In the second step, this complex either dissociates directly to $[CH_2Cl]^+ + H^+$ or

rearranges to the dication H_2CClH^{2+}. The pathways following the direct dissociation are summarized in Scheme 1, whereas the pathways that lead to other dissociations via rearrangement are summarized in Scheme 2.

3.3.1. "Loosely Bound" Intermediates. First, the formation of the loosely bound complexes will be discussed. The H_2 molecule can attack the dication $HCCl^{2+}$ at two sites, either at the C atom or at the Cl atom. Attack at the carbon site leads to the intermediate H_2HCCl^{2+} (**M9**). The two newly formed C−H bonds are longer (1.34 Å) than the original C−H bond (1.10 Å). This dication was described earlier by Duflot et al.,[6] and the corresponding CASSCF calculated geometry is given in parentheses in Figure 1a. The H_3CCl^{2+} structure with three equivalent C−H bonds exists as a stationary point in its triplet state (**M9***); the excitation energy is 1.10 eV. The intermediate H_2HCCl^{2+} (**M9**) can eliminate directly one proton via the transition state (**TS2**, Scheme 1): through the asymptotic mode, one of the distant H atoms gets closer to the C atom, whereas the other H atom is removed as a proton. The barrier height of this process is 0.90 eV. The barrier height of the competing process, which is the rearrangement to the H_2CClH^{2+} intermediate (**M10**) through the transition state **TS3** (Scheme 2), is only 0.66 eV. This barrier is 0.24 eV (∼30%) lower than the barrier for direct dissociation; therefore, the rearrangement via **TS3** may be expected to proceed more efficiently.

An attack of H_2 at the Cl site of $HCCl^{2+}$ (**M1**) results in the formation of the intermediate $HCCl-H_2^{2+}$ (**M11**). The distances of both H atoms to the Cl atom are rather large: 2.49 and 2.55 Å, respectively. Not surprisingly, the H_2 molecule bound to the Cl atom is only slightly perturbed; the length of the H−H bond is 0.76 Å, which is quite close to the equilibrium distance of an isolated molecule H_2. The intermediate **M11** loses one proton via the transition state **TS4**. The barrier height for the formation of the anti-isomer via ***anti*-TS4** is 2.14 eV, and the barrier height for the formation of the syn-isomer via ***syn*-TS4** is 2.36 eV. The removal of the H atom that is bonded to the C atom, and the subsequent formation of $CClH_2^+$ (**M7**), can be neglected. This reaction is very endoergic (3.59 eV); thus, it was not accessible under the conditions of the performed experiments (the collision energy was ≤2.16 eV).

The other isomer of the reactant dication, $CClH^{2+}$ (**M3**), also can be attacked at two sites. An attack of the H_2 molecule at the C site results in the formation of the intermediate H_2-CClH^{2+} (**M12**), where the incoming H_2 molecule is bound via one H atom to a C atom. Again, two rotamers (anti- and syn-) were found and the following analysis is given only for the anti-isomer. The surface of the syn-isomer shows analogous features and the corresponding values can be found in Tables 1 and 2. The structure **M12** was found as a true minimum with all frequencies being real at the CCSD(T)/6-31++G** level. Increasing the basis set to cc-pVTZ led to a rearrangement to the ylide dication H_2CClH^{2+} (**M10**). A quick check of the size of the basis set dependence for the intermediate **M12** was made on the B3LYP level with basis sets 6-31G**, 6-31++G**, 6−311G**, 6-311++G(3dp,3df), cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ, as implemented in Gaussian 98. A minimum for the intermediate **M12** was found only with the smallest 6-31G** and 6-31++G** basis sets. When increasing the basis set to a triple-ζ quality, the structure **M12** could not be located as a stationary point. All calculations resulted in the structure H_2CClH^{2+} (**M10**). Nevertheless, a transition state, which represents the barrier for the "out-of-plane" rotation of the H_2 molecule bound to the C atom (**TS5**), could be identified, using the CCSD(T)/cc-pVTZ method. The length of the H−H bond was, in this case, 0.84 Å and the distance from the center of the H−H bond to the C atom was 1.51 Å. The energy values in Tables 1 and 2, and Schemes 1 and 2 for **M12** correspond to the CCSD(T)/cc-pVTZ single-point energy calculation for the CCSD(T)/6-31++G** optimized structure. The ZPE was also derived from the CCSD(T)/6-31++G** calculations. The rotational barrier (**TS5**) has a slightly lower energy (by 0.02 eV) than the energy obtained in this way for **M12**. Therefore, the existence of **M12** seems to be highly questionable. This implies that the intermediate **M12** is, very likely, a shoulder on the relevant PES, rather than a distinct minimum, and that it rearranges to the intermediate H_2CClH^{2+} (**M10**). Consequently, the optimization the corresponding transition state (**TS6**) for this rearrangement is associated with similar difficulties. A transition state with a single imaginary frequency exists only at the CCSD(T)/6-31++G** level. The correct identification of the reaction path was checked by calculating the intrinsic reaction coordinate (IRC)[28] at the B3LYP/6-31++G** level. The barrier height is rather small (0.06 eV). When using the triple-ζ basis set (cc-pVTZ), either with the CCSD(T) or the B3LYP method, only a second-order transition state (**TS6′**) could be located in this area of the PES. The two imaginary frequencies were characterized as follows: one represents the desired mode (i.e., the same imaginary frequency as that observed for **TS6**), and the second represents an "out-of-plane" rotation of the H_2 fragment that is bonded to the C atom. The IRC calculations at the B3LYP/cc-pVTZ level lead to H_2CClH^{2+} (**M10**) in one direction and to the **TS5** in the other direction. The calculated barrier height was 0.01 eV. Finally, it could be concluded that **M12**, if existing at all, was only a very flat minimum, with a depth presumably below the ZPE.

The direct breakup of the intermediate $[H_2-CClH]^{2+}$ (**M12**) to the products $HCClH^+$ (**M8**) + H^+ proceeds via the transition state **TS7**, identified as a real transition state also at the CCSD(T)/cc-pVTZ level with a single imaginary frequency of *i*1118.5 cm^{-1} (***anti*-TS7**) and *i*927.7 cm^{-1} (***syn*-TS7**), characterizing the proper PES curvature. The barrier height calculated for the formation of ***anti*-M8** (with ***anti*-TS7**) was 0.92 eV, and that which was calculated for the formation of ***syn*-M8** (with ***syn*-TS7**) was 0.52 eV.

The isomer $CClH_2^+$ (**M7**), which is lying at a rather high energy, should be formed by an attack of the H_2 molecule at the Cl end of the $CClH^{2+}$ reactant. However, all attempts to optimize its structure with the proper connectivity, i.e., with all three H atoms bound to the Cl atom, led to dissociation of the C−Cl bond.

3.3.2. Dissociation of the Dication H_2CClH^{2+} (M10). The intermediate H_2CClH^{2+} (**M9**) can lose a proton either from the C atom or from the Cl atom. Breaking the Cl−H bond is less demanding, from an energy standpoint. In addition to the proton, the product ion H_2CCl^+ (**M6**) is formed in this dissociation process. The respective transition state **TS8** is connected with a barrier height of 2.09 eV.

The process, which requires more energy and the breaking of the C−H bond, leads to the product pair $HCClH^+ + H^+$. Again, the breaking of the C−H bond may occur in the syn-periplanar or anti-periplanar position, with respect to the C−Cl bond. Breaking the syn-periplanar C−H bond (***anti*-TS9**) leads to the anti-isomer (***anti*-M8**), and the barrier height is 4.59 eV. The optimized transition-state structures have rather long C−H bonds: 3.26 Å in the ***anti*-TS9** and 3.27 Å in the ***syn*-TS9** (Figure 1). Thus, the barrier height for breaking the anti-periplanar C−H bond is as large as the barrier height for breaking the syn-periplanar C−H bond (4.59 eV).

3.3.3. Application to Experimental Data. Theoretical information on the reactants, intermediates, transition states, and products, as well as on the calculated reaction pathways, was then applied to the available experimental data on the reaction $CHCl^{2+} + D_2$.[4,10] The ion product CD_2Cl^+ could not be identified among the reaction products (its intensity was beyond the limit of detection, i.e., <20% of the intensity of the product $CHDCl^+$).[10] Therefore, the pathways that lead either to this product or to a mixture of $CHDCl^+$ and CD_2Cl^+ were excluded from these considerations. The relative translational-energy distribution of the products $CHDCl^+ + D^+$ is characterized by two peaks in the $P(T')$ vs T' dependence (see Figure 2c). The major peak lies at ~4.7 eV. The analysis of the scattering results indicated that the products connected with this translational-energy release were formed by a decomposition of a short-lived intermediate of a mean lifetime of $\sim 10^{-12}$ s. The second process is characterized by a translational-energy release of ~1.1 eV, and the relevant portion of the scattering suggested that the product was formed via a decomposition of a long-lived complex intermediate of a mean lifetime that is considerably longer than $\sim 10^{-12}$ s.

The measured translational-energy release of processes that are associated with the decomposition of the intermediates can be related to the exit barrier heights on the way from the transition state to the products. All pathways shown in Scheme 1 (a, b, c), i.e., direct dissociation of "loosely bound" intermediates, lead to $CHDCl^+$. The common step in these processes is the formation of the complex $[D_2-CHCl]^{2+}$; in the next step, one D atom is bonded to the C or Cl atom and the other leaves as D^+. "Loosely bound" intermediates represent short-lived complexes. The exit barrier heights for pathways a and c are 4.06 and 3.33 eV, respectively. After including the collision energy (2.16 eV), the resulting values match the upper portion of the $P(T')$ curve in Figure 2c reasonably well, in the range from ~3.5 eV to 8 eV, with a maximum at ~5 eV.

The pathways that lead through the intermediate H_2CClH^{2+} (**M10**) had to be analyzed individually. The reaction of $HCCl^{2+}$ with D_2 will primarily result in the formation of the complex D_2-CHCl^{2+} (**M9**), which rearranges to $DHCClD^{2+}$ (**M10**), with one D atom being bound to the C atom and the other being bound to the Cl atom. This mechanism was confirmed by an IRC calculation from the transition state **TS3** at the B3LYP/cc-VTZ level. This intermediate will lose D^+ from the Cl atom more efficiently via the transition state **TS8** (pathway d), because the activation barrier is 2.50 eV, which is >50% lower than the activation barrier for dissociation via **TS9** (see pathway e). The transition state **TS9** is associated with the hydrogen loss from the C atom; thus, it would lead to a mixture of two products: $HDCCl^+$ and D_2CCl^+. This is, however, in conflict with the experimental observation.

The reaction of the other isomer, $CClH^{2+}$, with deuterium leads eventually to the complex $[D_2-CClH]^{2+}$ (**M12**), which, in the next step, rearranges to D_2CClH^{2+} (**M10**), with both D atoms being bonded to the C atom. Dissociation via the lower transition state **TS8** (pathway d) leads to a loss of the proton from the Cl atom and to the formation of the product D_2CCl^+. To explain why this product is not experimentally observed, one must realize that, at the collision energy of 2.16 eV, the total excess energy—with respect to the minimum **M10**—is 7.79 eV. If the D_2CCl^+ were formed via pathway d, it would possess a very large internal energy that would very likely lead to its dissociation (see Section 3.4). The pathway that leads through the transition state **TS9** (pathway e) with a much higher barrier leads to the product $DCClH^+$. However, because of the high barrier height, this process is less likely.

The ylide intermediate represents a long-lived complex; however, the exit barrier height for pathway d, 3.58 eV (3.69 eV, including the ZPE), is larger than the experimentally observed energy release (1.1 eV). However, the ylide intermediate possesses a rather high internal excitation; thus, it seems that this process may lead to the formation of an electronic excited state of the product $DHCCl^+$. An excited state of H_2CCl^+ was calculated to lie 3.18 eV above the ground state, and this value would fit the experimental results reasonably well.

3.4. Further Decomposition of CH_2Cl^+. The cation CH_2Cl^+ can decompose via a loss of a H_2 molecule:

$$CH_2Cl^+(\mathbf{M6}) \rightarrow CCl^+(\mathbf{M5}) + H_2 \qquad (\Delta E = -3.23\ \text{eV}) \quad (8)$$

This endoergic process proceeds via the transition state **TS10**, and the barrier height is 4.06 eV.

From the theoretical analysis and a comparison with the experimental data,[10] it was concluded that the low-energy peak in the relative translational-energy distribution of CCl^+ (see Figure 1b) originates from further decomposition of a vibrationally excited product $CHDCl^+$. As mentioned previously, the cation CD_2Cl^+, which is formed in the reaction of $CClH^{2+}$ with D_2 via the decomposition of the intermediate D_2CClH^{2+}, should possess a large internal excitation; thus, it could easily decompose to CCl^+ and D_2. However, this cannot be proven experimentally, because the product CD_2Cl^+ could not be observed in measurable amounts.

4. Heats of Formation

The present study makes it possible to estimate the heats of formation, $\Delta_f H$, of the species CH_xCl^{n+} (where $x = 0, 1, 2$ and $n = 1, 2$) involved. For the cations, related published experimental data can be used in the derivation. For the dications, the estimation was based on enthalpies of reactions as described in this paper. The data and reactions used are summarized in Table 3.

The heat of formation of the cation $HCCl^+$, $\Delta_f H°(HCCl^+) = 1284$ kJ/mol, was determined from the published data for the carbene HCCl ($\Delta_f H°(HCCl) = 334.7$ kJ/mol,[29] IE(HCCl) = 9.84 eV[30]). In a similar way, the heat of formation of CCl^+, $\Delta_f H°(CCl^+) = 1360$ kJ/mol, was obtained from $\Delta_f H°(CCl) = 502$ kJ/mol[29] and IE(CCl) = 8.9 ± 0.2 eV.[31] For H_2CCl^+, the heat of formation was determined as a sum of $\Delta_f H°(H_2CCl^-)$ (66.3 kJ/mol[32]), IE(H_2CCl) (8.75 ± 0.01 eV[33]), and the electron affinity of H_2CCl (0.74 ± 0.16 eV[34]); $\Delta_f H°(H_2CCl^+) = 982$ kJ/mol.

The estimation of heats of formation of ions in Table 3 was based on reactions in which these ions are produced from cations of known $\Delta_f H°$, as obtained previously (CCl^+, $HCCl^+$, and H_2CCl^+), and tabulated data for $\Delta_f H°(H) = 218$ kJ/mol, and $\Delta_f H°(H^+) = 1530$ kJ/mol.[35] For calculation of the reaction enthalpies ($\Delta_r H$), the values of E_0(G2) energies and ϵ_0(CCSD(T)) were used as given in Table 1. The values of $\Delta_r H$ corrected for ZPE ($\epsilon_0 + \epsilon_{ZPE}$) and the values that had been corrected for internal thermal energy (E_{tr}, E_{rot}, E_{vib}, E_e) and the factor k_bT, implemented in the Gaussian 98 as a thermal correction to the enthalpy H_{corr},[18] also were tested. The tests were conducted for calculations of the $\Delta_f H°$ values of CCl^+, $HCCl^+$, and H_2CCl^+ (see the upper portion of Table 3). The values of $\Delta_r H$ that were calculated from ϵ_0 led to the best agreement with the experimental data and the smallest error of the mean. Using the E_0 (G2) energies (Table 1), the heat of formation of the dication

TABLE 3: Estimation of Heats of Formation ($\Delta_f H$)[a] of the Dications $HCCl^{2+}$ and $CClH^{2+}$ and the Cations $CClH^+$ and $HCClH^+$

ion	equation	$\Delta_f H$ calculated from tabulated data (kJ/mol)
CCl^+	$\Delta_f H(CCl) + IE(CCl)$	1360.80 ± 19.30
$HCCl^+$	$\Delta_f H(HCCl) + IE(HCCl)$	1284.14
H_2CCl^+	$\Delta_f H(H_2CCl^-) + EA(H_2CCl) + IE(H_2CCl)$	981.97

		CCSD(T)		G2	
ion	reaction	estimated $\Delta_f H$ (kJ/mol)	average ± SEM[b]	estimated $\Delta_f H$ (kJ/mol)	average ± SEM[b]
CCl^+	$H_2CCl^+ \rightarrow CCl^+ + H_2$	1327.9		1293.8	
	$HCCl^+ \rightarrow CCl^+ + H$	1372.6	1350.3 ± 18.2	1348.3	1321.0 ± 22.3
$HCCl^+$	$H_2CCl^+ \rightarrow HCCl^+ + H$	1256.9		1228.8	
	$H + CCl^+ \rightarrow HCCl^+$	1272.3	1264.6 ± 6.3	1296.6	1262.7 ± 27.7
H_2CCl^+	$HCCl^+ + H \rightarrow H_2CCl^+$	1009.2		1037.3	
	$CCl^+ + H_2 \rightarrow H_2CCl^+$	1014.8	1012.0 ± 2.3	1049.0	1043.2 ± 4.8
$HCCl^{2+}$	$HCCl^+ \rightarrow HCCl^{2+}$	2961.3		2961.6	
	$H_2CCl^+ \rightarrow HCCl^{2+} + H^-$	3016.1	2975.5 ± 20.6	2982.2	2972.4 ± 6.0
	$H^+ + CCl^+ \rightarrow HCCl^{2+}$	2949.2		2973.4	
$CClH^{2+}$	$CClH^+ \rightarrow CClH^{2+}$	3257.5		3253.3	
	$H^+ + CCl^+ \rightarrow CClH^{2+}$	3245.4	3271.7 ± 20.6	3265.0	3264.0 ± 6.0
	$H_2CCl^+ \rightarrow CClH^{2+} + H^-$	3312.3		3273.8	
$CClH^+$	$HCCl^+ \rightarrow CClH^+$	1523.1		1525.6	
	$H + CCl^+ \rightarrow CClH^+$	1511.2	1510.1 ± 7.9	1538.1	1511.4 ± 20.8
	$H_2CCl^+ \rightarrow CClH^+ + H$	1495.8		1470.3	
$HCClH^+$	$HCCl^+ + H \rightarrow HCClH^+$	1334.4		1355.5	
	$CCl^+ + H_2 \rightarrow HCClH^+$	1340.1	1327.3 ± 10.2	1367.2	1341.0 ± 20.7
	$H_2CCl^+ \rightarrow HCClH^+$	1307.2		1300.2	

[a] $\Delta_f H$ values for CCl^+, $HCCl^+$, and H_2CCl^+ were calculated from tabulated data.[29−34] [b] SEM = standard error of the mean.

$HCCl^{2+}$ is $\Delta_f H°(HCCl^{2+}) = 2972 \pm 6.0$ kJ/mol, and the heat of formation of the isomer dication $CClH^{2+}$ is $\Delta_f H°(CClH^{2+}) = 3264 \pm 6.0$ kJ/mol. The calculations give $\Delta_f H°(CClH^+) = 1511 \pm 20$ kJ/mol, for the heat of formation of the isomer cation $CClH^+$, and finally $\Delta_f H°(HCClH^+) = 1341 \pm 21$ kJ/mol (which is the value for the anti-isomer).

5. Conclusions

(1) The potential energy surface of the $CHCl^{2+} + D_2$ system was investigated using the CCSD(T)/cc-pVTZ method, to determine the reaction pathways that lead to the experimentally observed products $CHCl^+$, $CHDCl^+$, and CCl^+.

(2) The product $CHCl^+$ was determined to be the product of a nondissociative charge-transfer process between the two isomers of $CHCl^{2+}$ ($HCCl^{2+}$ and $CClH^{2+}$) and D_2. The main contribution comes from the ground and first excited state of $CClH^{2+}$, giving the ground state of $CClH^+ + D_2^+$ (with calculated exoergicities of 2.42 and 4.50 eV, respectively). The contribution of charge transfer with the ground state of $HCCl^{2+}$ (with an exoergicity of 1.90 eV) is minor.

(3) The product CCl^+ results mainly from a proton-transfer reaction between the ground state of $HCCl^{2+}$ and D_2 and leads to CCl^+ and D_2H^+(exoergicity of 5.30 eV). The proton-transfer reaction with the ground state of $CClH^{2+}$ (exoergicity of 8.32 eV) also may contribute to the formation of the products. The calculated reaction pathways are in agreement with the experimental data.

(4) In the chemical reaction of $CHCl^{2+}$ with H_2, which leads to the products $[CH_2Cl]^+ + H^+$, the formation of two isomers of the molecular product—H_2CCl^+ and $HCClH^+$—was investigated. With the reactant dication $HCCl^{2+}$, the formation of H_2CCl^+ is associated with an exoergicity of 4.09 eV, and the formation of $HCClH^+$ is associated with an exoergicity of 0.79 eV. With the reactant dication $CClH^{2+}$, the respective exoergicities are 7.11 eV for the formation of H_2CCl^+, and 3.81 eV for the formation of $HCClH^+$. In general, two types of pathways lead to the product formation. One leads directly to the reaction products through a loosely bound complex ($[H_2-CHCl]^{2+}$). The other one involves the formation of a "stable" intermediate H_2CClH^{2+}, which can dissociate to the products either by losing a proton from the Cl atom or by losing a proton from the C atom (a less likely case).

(5) A dissociation pathway for the formation of $H_2CCl^+ + H^+$ also was observed. This pathway was associated with a process that was endoergic by 3.23 eV.

(6) Using the calculated data and published thermodynamic information on several cations, the heats of formation of the dication isomers $HCCl^{2+}$ and $CClH^{2+}$, and those of the cations $CClH^+$ and $HCClH^+$, were estimated.

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