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Matrix Isolation Fourier Transform Infrared Spectroscopic and Density Functional Theoretical Studies of the Reactions of Chromium Atoms and Acetylene

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The reactions between chromium atoms and acetylene have been investigated in solid argon with infrared absorption spectroscopy. It is found that the ground-state chromium atoms reacted with acetylene to form the metallocyclopropene $Cr(C_2H_2)$ molecule spontaneously on annealing. The $Cr(C_2H_2)$ molecule underwent photochemical rearrangement to the alkynyl hydride HCrCCH molecule upon ultraviolet−visible irradiation. The two products were identified on the basis of isotopic IR studies with $^{13}C_2H_2$ and C_2D_2, and density functional theory calculations.

Introduction

The interactions of transition metal atoms with acetylene have received considerable attention. The breadth of investigation includes low-temperature matrix isolation spectroscopic studies,[1−6] gas-phase kinetic experiments [7,8] and quantum chemical theoretical computations.[9−14] Ozin et al.[1] have investigated the interactions of nickel and copper atoms with acetylene in solid matrixes using infrared and UV−visible absorption spectroscopies; the metal−acetylene complexes with π coordinated structure (C_{2v} symmetry) consistent with the Dewar−Chatt−Duncansan scheme of bonding have been identified. Matrix isolation electron spin resonance studies also indicated that C_{2v} π complexes were formed for copper and gold atom reactions.[2,3] Gas-phase kinetic studies showed that the copper monoacetylene complex is thermally unstable at 295 K and either dissociates or adds a second acetylene to form the stable copper bisacetylene complex.[7] However, nickel atoms formed strongly bound π complexes with acetylene; the binding energy was estimated to be 46 kcal/mol.[8] Margrave and co-workers[4] have reported that iron atoms cocondensed with acetylene in solid matrix formed an iron−hydrogen-bonded Fe−HCCH complex, and upon UV photolysis, the iron atom was inserted into a C−H bond of acetylene to give HFeCCH. The same group reported that the nickel atom formed a π complex with acetylene. This π complex photorearranged upon visible photolysis with the formation of nickel vinylidene, $NiCCH_2$.[5] A similar π complex has been predicted for a manganese−acetylene adduct with ab initio calculations.[9] The structure and EPR parameters of CuC_2H_2 have been investigated by local and gradient-corrected density functionals.[10] The computed hyperfine coupling constants are in good agreement with experiment only for the C_{2v} structure, whereas a vinylic C_s structure is more stable according to theoretical calculations. This vinylic C_s structural radical has been observed in silver and gold reactions with acetylene.[3,6]

It is noteworthy that the previous studies of transition metal atom−acetylene reactions were focused on later transition metals, yet no investigations involving early transition metals were reported. As can be seen from the literature studies, the later transition metal−acetylene systems exhibited quite different reaction mechanisms. Therefore, it is quite interesting to study the chemistry of other transition metal atoms with acetylene. In particular, the combination of experimental and theoretical approaches is extremely beneficial in understanding and interpreting the reaction mechanisms. Here we report a combined matrix isolation Fourier transform infrared (FTIR) spectroscopic and theoretical investigation on the reactions of chromium atoms with acetylene. We will show that the ground-state chromium atoms reacted with acetylene in solid argon matrix to form the $Cr(C_2H_2)$ metallocyclopropene spontaneously on annealing, while photoisomerism to form the HCrCCH alkynyl hydride molecule proceeded upon UV−visible photolysis.

Experimental and Theoretical Methods

The experimental setup for pulsed laser ablation and matrix infrared spectroscopic investigation has been described previously.[15] Briefly, the 1064 nm Nd:YAG laser fundamental (Spectra Physics, DCR 150, 20 Hz repetition rate and 8 ns pulse width) was focused onto the rotating chromium metal target through a hole in a CsI window. Typically, 5−10 mJ/pulse laser energy was used. The ablated metal atoms were codeposited with acetylene in excess argon onto the 11 K CsI window, which was mounted on a cold tip of a closed-cycle helium refrigerator (Air Products, Model CSW202) for 1 h at a rate of approximately 4 mmol/h. Acetylene was subjected to several freeze−pump−thaw cycles to minimize possible atmospheric contamination. The isotopic $^{13}C_2H_2$ and C_2D_2 (99%, Cambridge Isotopic Laboratories) and selected mixtures were used in different experiments. Infrared spectra were recorded on a Bruker IFS113V spectrometer at 0.5 cm^{-1} resolution with a DTGS detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to broadband photolysis by use of a 250 W high-pressure mercury arc lamp with the globe removed.

Density functional calculations were performed with the Gaussian 98 program.[16] The three-parameter hybrid functional according to Becke with additional correlation corrections due to Lee, Yang, and Parr was utilized (B3LYP).[17,18] This hybrid functional can provide very reliable predictions of the state energies, structures, and vibrational frequencies of transition

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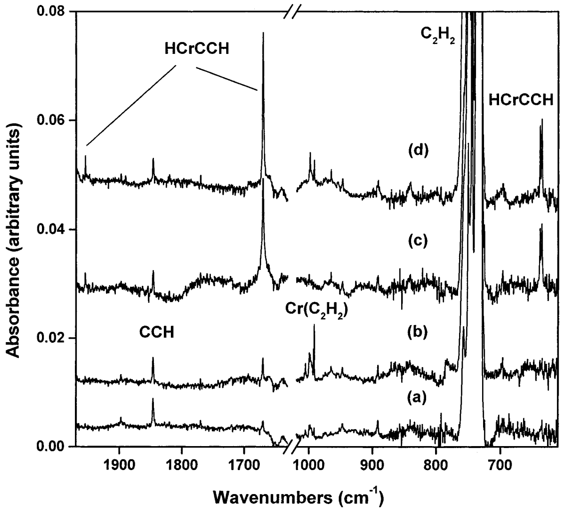

Figure 1. Infrared spectra in the 1970−1630 and 1020−610 cm^{-1} regions from codeposition of laser-ablated chromium atoms and 0.2% C_2H_2 in argon: (a) 1 h sample deposition at 11 K, (b) after 25 K annealing, (c) after 20 min of broadband photolysis, and (d) after 28 K annealing.

TABLE 1: Infrared Absorptions[a] from Codeposition of Laser-ablated Chromium Atoms with Acetylene in Excess Argon

$^{12}C_2H_2$	$^{13}C_2H_2$	$^{12}C_2D_2$	assignment
1955.2	1885.2	1844.3	HCrCCH, C−C stretching
1670.1	1670.1	1204.4	HCrCCH, Cr−H stretching
1476.4	1423.6	1422.4	$Cr(C_2H_2)$, C−C stretching
991.9	977.4		$Cr(C_2H_2)$, out-of-plane CCH deformation
638.4	632.6		HCrCCH, CCH bending
635.5	629.9		HCrCCH, CCH bending

Infrared absorptions are given in reciprocal centimeters.

metal-containing compounds.[19−21] The 6-311++G(d,p) basis sets were used for H and C, and the all-electron basis set of Wachters and Hay as modified by Gaussian was used for Cr.[22,23] The geometries were fully optimized, harmonic vibrational frequencies were calculated with analytic second derivatives, and zero-point vibrational energies (ZPVE) were derived. Transition-state optimizations were done with the synchronous transit-guided quasi-Newton (STQN) method at the B3LYP/6-311++G(d,p) level.[24]

Results and Discussion

Infrared Spectra. The laser ablation technique was employed to produce chromium metal atoms. This technique has proven to be a very powerful method in generating high melting point metal atoms for matrix isolation studies.[25,26] Figure 1 shows the representative spectra in selected regions from codeposition of laser-ablated chromium atoms with acetylene in excess argon, and the product absorptions are listed in Table 1. Sample deposition for 1 h at 11 K reveals strong C_2H_2 absorptions and weak CCH and CCH^- absorptions.[27] New product absorptions at 1476.4 and 991.9 cm^{-1} were produced on annealing. A 20 min broadband photolysis destroyed the 1476.4 and 991.9 cm^{-1} absorptions and produced a set of new absorptions at 1955.2, 1670.1, 638.4, and 635.5 cm^{-1}.

Similar experiments were done with $^{13}C_2H_2$ and C_2D_2, and the shifted bands are reported in Table 1. Analogous investigations with $^{12}C_2H_2 + {}^{13}C_2H_2$ and $C_2H_2 + C_2D_2$ mixed isotopic samples gave important diagnostic multiplets. Isotopic spectra in selected regions are compared in Figures 2 and 3.

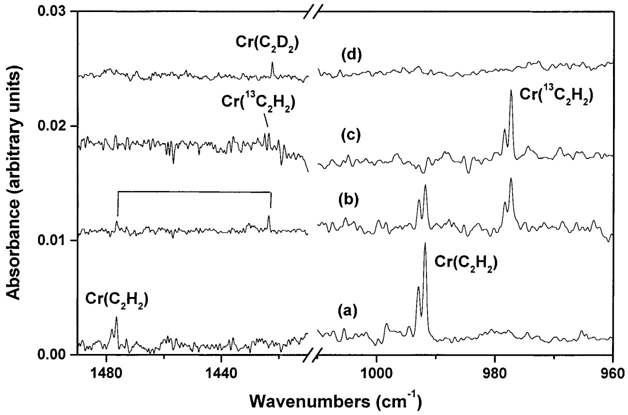

Figure 2. Infrared spectra in the 1490−1410 and 1010−960 cm^{-1} regions from codeposition of laser-ablated chromium atoms with different isotopic samples in excess argon and annealed to 25 K: (a) 0.2% C_2H_2, (b) 0.1% $^{12}C_2H_2$ + 0.1% $^{13}C_2H_2$, (c) 0.2% $^{13}C_2H_2$, and (d) 0.2% C_2D_2.

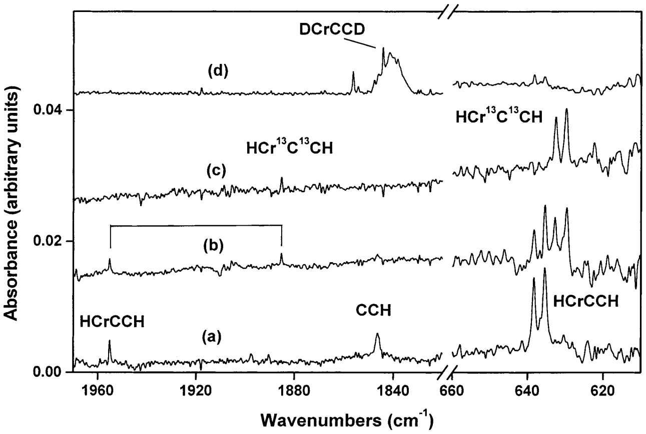

Figure 3. Infrared spectra in the 1970−1820 and 660−610 cm^{-1} regions from codeposition of laser-ablated chromium atoms with different isotopic samples in excess argon. Spectra were recorded after 20 min photolysis and then annealed to 28 K: (a) 0.2% C_2H_2, (b) 0.1% $^{12}C_2H_2$ + 0.1% $^{13}C_2H_2$, (c) 0.2% $^{13}C_2H_2$, and (d) 0.2% C_2D_2.

Calculation Results. Three CrC_2H_2 isomers are considered theoretically, namely, the $Cr(C_2H_2)$ adduct with C_{2v} symmetry, the HCrCCH insertion molecule, and the chromium vinylidene ($CrCCH_2$) molecule. The optimized ground-state structures are shown in Figure 4. All three isomers were predicted to have quintet ground states and are quite close in energy. The $^5B_2$ $Cr(C_2H_2)$ molecule is the global minimum at this level of theory. The $^5A'$ HCrCCH insertion molecule is 2.9 kcal/mol higher in energy than $Cr(C_2H_2)$, and the vinylidene $CrCCH_2$ ($^5B_2$) is 4.7 kcal/mol less stable than $Cr(C_2H_2)$.

$Cr(C_2H_2)$. The bands at 1476.4 and 991.9 cm^{-1} can be grouped together on the basis of their growth/decay characteristics measured as a function of changes of experimental conditions. The 1476.4 cm^{-1} band shifted to 1423.6 cm^{-1} with $^{13}C_2H_2$, and to 1422.4 cm^{-1} with C_2D_2, and gave isotopic frequency ratios of 1.0371 ($^{12}C/^{13}C$) and 1.0380 (H/D). The $^{12}C/^{13}C$ ratio indicated that the 1476.4 cm^{-1} band should be assigned to a C−C stretching vibration. No obvious intermediate was observed in the experiment with the mixed $^{12}C_2H_2 + {}^{13}C_2H_2$ sample, suggesting that the molecule contains only one C_2H_2. The experiments employed relatively low ablation laser energy, so the possibility for the formation of multimetal species is low, suggesting that most likely only one chromium atom is involved in this molecule. Therefore, we assign the 1476.4 cm^{-1} band to a $Cr(C_2H_2)$ adduct. The 991.9 cm^{-1} band shifted to 977.4

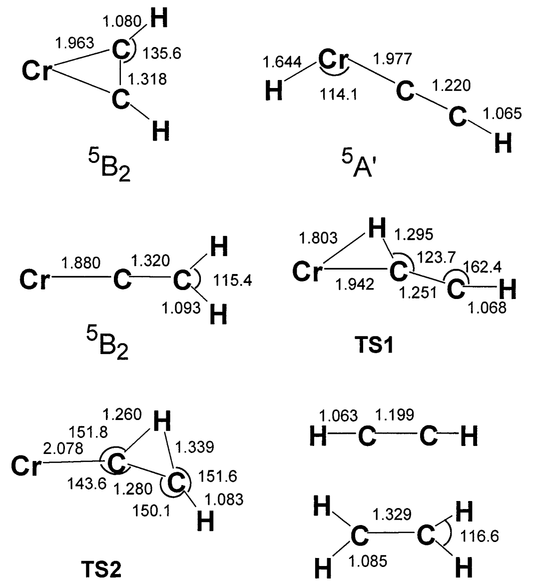

Figure 4. Optimized structures (bond lengths in angstroms, bond angles in degrees) of three CrC_2H_2 isomers and the transition states on the potential energy surfaces.

TABLE 2: Calculated (B3LYP/6-311++G(d,p)) Vibrational Frequencies and Intensities of $Cr(C_2H_2)$ ($^5B_2$)^a

$Cr(C_2H_2)$	$Cr(^{13}C_2H_2)$	$Cr(C_2D_2)$	mode
540.4 (49.0)	526.2 (44.8)	475.5 (54.1)	antisymm Cr−C stretching
540.5 (17.9)	527.6 (16.8)	479.0 (54.1)	symm Cr−C stretching
632.0 (75.6)	628.5 (73.7)	512.2 (19.2)	C_2H_2 tilt
816.5 (7.7)	814.7 (8.3)	607.2 (0.2)	CCH deformation
862.2 (0.0)	852.7 (0.0)	691.3 (0.0)	C_2H_2 torsion
992.7 (97.7)	978.0 (99.0)	835.2 (41.2)	CCH deformation
1532.4 (18.8)	1476.5 (17.1)	1465.9 (19.3)	C−C stretching
3112.0 (17.8)	3103.0 (18.3)	2284.6 (6.6)	antisymm C−H stretching
3148.2 (20.5)	3135.4 (21.8)	2366.8 (3.2)	symm C−H stretching

Vibrational frequencies are given in reciprocal centimeters; intensities (in parentheses) are given in kilometers per mole. The vibrational frequencies of C_2H_2 were calculated at 3522.8 cm^{-1} (0 km/mol, σ_g), 3420.2 cm^{-1} (94 km/mol, σ_u), 2061.9 cm^{-1} (0, σ_g), 773.0 cm^{-1} (222 km/mol, π_u), and 661.2 cm^{-1} (0 km/mol, π_g).

cm^{-1} with $^{13}C_2H_2$ and is due to the CCH deformation mode. Due to isotopic effect, the CCD deformation mode was too weak to be observed.

The assignment was strongly supported by DFT calculations. As shown in Figure 4 and Table 2, the $Cr(C_2H_2)$ adduct was predicted to have a $^5B_2$ ground state with C_{2v} symmetry. The C−C stretching and CCH deformation modes were computed at 1532.4 and 992.7 cm^{-1}, respectively, which are in good agreement with the experimental frequencies. The isotopic frequency ratios calculated for each mode ($^{12}C/^{13}C$, 1.0379 and 1.0150; H/D, 1.0454 and 1.1886) also fit the experimental values very well. The C_{2v} $Cr(C_2H_2)$ molecule would have nine vibrations (as listed in Table 2); besides the above characterized C−C stretching and CCH deformation modes, the symmetric and antisymmetric C−H stretchings, the HCCH tilt, and the symmetric and antisymmetric Cr−C stretching modes were predicted to have appreciable intensities. However, we were not able to observe these bands. One possible explanation is that DFT calculations overestimated the intensities of these vibrational modes. As a reference point, DFT calculations also overestimated some absorptions such as C−H stretching of vinyl titanium hydride in a recent study on the reaction of titanium and ethylene.[28]

The C−C stretching vibrational frequency of $Cr(C_2H_2)$ at 1476.4 cm^{-1} is about 497 cm^{-1} red-shifted from the C−C stretching frequency of acetylene and is about 152 cm^{-1} lower than the C−C stretching frequency of ethylene.[29] This C−C stretching frequency is significantly lower than that of other reported transition metal−acetylene π complexes, $Ni(C_2H_2)$ (1647.4 cm^{-1})[5] and $Cu(C_2H_2)$ (1870 cm^{-1}),[1] and is very close to the value of titanacyclopropene $H_2Ti(C_2H_2)$ in solid argon (1464.8 cm^{-1}).[28] This implies that $Cr(C_2H_2)$ is not a π complex but should be considered as a metallocyclopropene. The theoretically predicted Cr−C, C−C, and C−H bond lengths of $Cr(C_2H_2)$ are 1.963, 1.318, and 1.080 Å, respectively. Compared to free acetylene, the C−C and C−H bond lengths increase by about 0.119 and 0.017 Å, and the C−H bonds move out of the CC axis and away from the Cr atom. The NBO analysis shows that $Cr(C_2H_2)$ has two Cr−C σ bonds and a C−C double bond.

The frequency of C−C stretching vibration of $Cr(C_2H_2)$ is lower than some experimentally characterized transition metal carbonyl−acetylene complexes. The $M(CO)_5(C_2H_2)$ and $M(CO)_4(C_2H_2)$ (M = Mo or W) molecules have been recently observed in solid matrixes.[30,31] The C−C stretching vibrations of $Mo(CO)_5(C_2H_2)$ and $W(CO)_5(C_2H_2)$ were observed at 1822 and 1774 cm^{-1}, respectively. Frenking and co-workers[32] have theoretically studied $M(CO)_5(C_2H_2)$ (M = Cr, Mo, or W). These molecules were predicted to be Dewar−Chatt−Duncanson-type complexes with quite long $(CO)_5M-C$ bond lengths (2.275 Å for Cr, 2.368 Å for Mo, and 2.331 Å for W). However, $Mo(CO)_4(C_2H_2)$ and $W(CO)_4(C_2H_2)$ showed much lower C−C stretching frequencies (1670 cm^{-1} for Mo and 1522 cm^{-1} for W), indicating that acetylene binds more strongly to tetracarbonyls than pentacarbonyls.[31]

HCrCCH. One set of new product bands at 1955.2, 1670.1, 638.4, and 635.5 cm^{-1} appeared together on broadband photolysis at the expense of the $Cr(C_2H_2)$ absorptions. These bands are assigned to the HCrCCH molecule on the basis of isotopic substitutions and DFT calculations. The 1670.1 cm^{-1} band showed no carbon-13 shift but was shifted to 1204.4 cm^{-1} with C_2D_2 and gave an isotopic H/D ratio of 1.3867. The band position as well as the isotopic H/D ratio is close to the values of the Cr−H stretching vibration of various previously characterized chromium hydrides, which implies that the 1670.1 cm^{-1} band is due to a Cr−H stretching vibration. For example, the Cr−H stretching vibration of the HCrOH molecule was observed at 1639.9 cm^{-1} with an H/D ratio of 1.3845.[33] That of HCrO(OH) was observed at 1753.1 cm^{-1} with an H/D ratio of 1.3831.[34] The 1955.2 cm^{-1} band shifted to 1885.2 cm^{-1} with $^{13}C_2H_2$. The isotopic $^{12}C/^{13}C$ ratio of 1.0371 is only slightly smaller than that of a pure C−C stretching vibration (1.0408). The 1955.2 cm^{-1} band should thus be assigned to a C−C stretching vibration mixing with some other vibrational components. The C_2D_2 counterpart was observed at 1844.3 cm^{-1} and gave an H/D ratio of 1.0601. The IR-inactive but Raman-active C−C stretching vibration of free acetylene was observed at 1973.8 cm^{-1} with the C_2D_2 counterpart at 1762.4 cm^{-1}.[4,5,29] Note that the H/D ratio of free acetylene (1.1200) is considerably larger than the ratio observed here for the 1955.2 cm^{-1} band. This suggests that there is less hydrogen involvement in the 1955.2 cm^{-1} mode than that in free acetylene, so most likely only one hydrogen atom is involved. The 638.4 and 635.5 cm^{-1} bands exhibited very small carbon-13 shifts (5.8 and 5.6 cm^{-1}, respectively); the deuterium counterparts were overlapped by the strong C_2D_2 absorptions. These two bands are assigned to the in-plane and out-of-plane CCH bending vibrations of HCrCCH.

To provide additional insight into the spectroscopic assignment of HCrCCH and to provide a prediction of its structure

TABLE 3: Calculated (B3LYP/6-311++G(d,p)) Frequencies and Intensities of HCrCCH($^5A'$)

HCrCCH	HCr^{13}C^{13}CH	DCrCCD	mode
176.6 (30.2)	169.4 (29.9)	156.5 (28.7)	
196.1 (22.5)	189.9 (20.0)	184.2 (29.6)	
422.1 (21.8)	415.4 (15.1)	336.7 (53.3)	
502.0 (228.0)	495.3 (232.0)	467.5 (105.5)	HCrC bending
677.8 (56.3)	671.7 (57.1)	534.2 (23.2)	out-of-plane CCH bending
701.6 (50.6)	695.1 (51.4)	554.6 (21.5)	in-plane CCH bending
1712.1 (197.9)	1712.1 (197.9)	1223.1 (105.4)	Cr−H stretching
2037.0 (20.4)	1963.7 (18.3)	1910.1 (31.8)	C−C stretching
3449.4 (43.2)	430.4 (43.4)	2658.3 (14.7)	C−H stretching

Vibrational frequencies are given in reciprocal centimeters; intensities (in parentheses) are given in kilometers per mole.

and bonding, we have turned to density functional calculations. As shown in Figure 4, we predicted that the HCrCCH molecule has a $^5A'$ ground state with planar structure, with Cr−H, Cr−C, C−C, and C−H bond lengths of 1.644, 1.977, 1.220, and 1.065 Å, respectively. The HCrC bond angle was predicted to be 114.1°, while the CrCCH unit is almost linear. The Cr−C bond is a single bond with a bond length very close to that in $Cr(C_2H_2)$. The C−C bond is a triple bond, which is only slightly longer (0.021 Å) than that in free acetylene. The calculated frequencies at the optimized geometry of HCrCCH provide excellent support for the assignment. As listed in Table 3, the C−C stretching, Cr−H stretching, and the in-plane and out-of-plane CCH bending vibrations of HCrCCH were calculated at 2037.1, 1713.3, 702.4, and 678.8 cm^{-1}, respectively (4.2%, 2.6%, 10.0%, and 6.8% higher). The DFT normal-mode analyses are consistent with the experimentally observed isotopic effects on the frequencies. The 1713.3 cm^{-1} band is a pure Cr−H stretching mode with no carbon coupling. The calculated isotopic frequency ratios of the C−C stretching modes: 1.0373 ($^{12}C/^{13}C$) and 1.0664 (H/D) fit well with the experimental values (1.0371 and 1.0601). The disagreement between theory and experiment is that we were not able to observe the C−H stretching and the HCrC bending vibrations, which were predicted to be relatively intense. As has been mentioned above, DFT calculations may overestimate the IR intensities of these modes. We note that the signal-to-noise ratios in these two spectral regions are lower, and weak absorptions are difficult to detect.

Reaction Mechanism. The spectra clearly showed that the absorptions due to $Cr(C_2H_2)$ increased upon annealing, suggesting that reaction 1 is exothermic with minimal activation energy. The HCrCCH absorptions were produced on broadband photolysis, during which the $Cr(C_2H_2)$ absorptions were diminished. It appears that broadband photolysis initiates insertion reaction 2.

$$Cr\ (^7P) + C_2H_2\ (^1\Sigma_g^{\ +}) \rightarrow Cr(C_2H_2)\ (^5B_2) \qquad \Delta E = -11.8\ \text{kcal/mol} \quad (1)$$

$$Cr(C_2H_2)\ (^5B_2) \rightarrow HCrCCH\ (^5A') \qquad \Delta E = +2.9\ \text{kcal/mol} \quad (2)$$

The isomerization of transition metal−alkyne complexes is an important process in transition metal-catalyzed alkyne reactions.[35] The vinylidene complex is frequently formed via rearrangement of the alkyne complex, and basically two reaction mechanisms have been proposed and extensively studied.[36] The direct 1,2-hydrogen migration proceeds via a transition state with a “slipping” alkyne ligand. The alternative rearrangement takes places via an alkynyl(hydrido) intermediate. In the studies of the photochemical behavior of matrix isolated $Mo(CO)_6$ and $W(CO)_6$ in the presence of alkynes, the vinylidene derivatives $(R)HCCM(CO)_5$ (R = H or CH_3, M = Mo or W) were formed on photolysis in addition to the η^2-alkyne complexes.[30,31] In present experimental conditions, the chromium and acetylene reaction yields only the metallocyclopropene $Cr(C_2H_2)$ and the alkynyl(hydrido) HCrCCH molecules; no further reaction product such as the vinylidene $CrCCH_2$ molecule was produced. DFT calculations predicted $CrCCH_2$ to have a $^5B_2$ ground state with C_{2v} symmetry, which is only about 4.7 kcal/mol higher in energy than the $Cr(C_2H_2)$ molecule. The theoretically predicted Cr−C and C−C bond lengths of $CrCCH_2$ (1.880 and 1.320 Å) indicate a Cr−C double bond and a C−C double bond. The calculated vibrational frequencies and intensities are listed in Table 4. The CH_2 deformation vibration at 878.4 cm^{-1} was predicted to be the most intense mode. The spectrum in this region is very clean and no product absorption is observed.

TABLE 4: Calculated (B3LYP/6-311++G(d,p)) Vibrational Frequencies and Intensities of $^5B_2$ $CrCCH_2$ and the Transition States on the Potential Energy Surfaces Shown in Figure 5

$CrCCH_2$ ($^5B_2$)	3080.5 (15, b_2), 3029.5 (41, a_1), 1626.4 (1, a_1), 1389.9 (0, a_1), 934.4 (7, b_2), 878.4 (50, b_1), 451.1 (26, a_1), 223.3 (42, b_1), 211.1 (37, b_2)
TS1	3150.0 (5), 2297.3 (404), 1647.2 (3187), 579.8 (3446), 405.1 (30), 309.1 (706), 198.0 (90), 182.6 (41), 1725.5i (2258)
TS2	3394.0 (31), 1811.6 (59), 1497.7 (60), 714.3 (35), 676.2 (179), 431.6 (23), 289.5 (101), 220.9 (37), 687.4i (482)

Vibrational frequencies are given in reciprocal centimeters; intensities (in parentheses) are given in kilometers per mole.

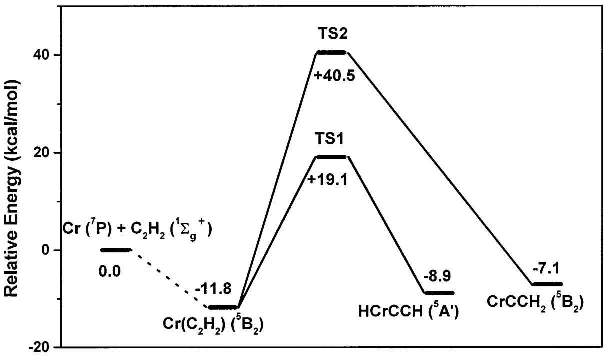

Figure 5. Potential energy profile for the chromium atom and acetylene reactions (energies given are in kilocalories per mole).

Figure 5 shows the potential energy profile for chromium atom reactions with acetylene. The ground-state ^7P chromium atom interacts with acetylene to form the $^5B_2$ state $Cr(C_2H_2)$; the reaction is exothermic by about 11.8 kcal/mol. Two transition states TS1 and TS2 have been located on the potential energy surfaces, which connect the equilibrium structure of $Cr(C_2H_2)$ with HCrCCH and $CrCCH_2$. The optimized transition-state structures are shown in Figure 4. TS1 is the transition state for reaction 2. This transition state lies 19.1 kcal/mol higher in energy than the ground-state reactants, Cr (^7P) + C_2H_2 ($^1\Sigma_g^{\ +}$); therefore, the energy barrier for reaction 2 is estimated to be 30.9 kcal/mol. TS1 has a nearly linear CCH structure with a C−C bond length of 1.251 Å. The Cr−C bond length (1.942 Å) is shorter than that in $Cr(C_2H_2)$ (1.963 Å) and HCrCCH (1.977 Å). This transition state structure is very different from the reported transition state for the corresponding rearrangement reaction, $F_4W(C_2H_2) \rightarrow F_4H(CCH)$.[36] In this reaction process, the transition state has a rather acute terminal CCH bonding angle (113.2°) and quite a long C−C bond length (1.363 Å).

The transition state TS2 connects the $Cr(C_2H_2)$ metallocyclopropene and the vinylidene $CrCCH_2$. The Cr−C bond distance of TS2 is clearly longer than that of $Cr(C_2H_2)$ and $CrCCH_2$, while the C−C bond distance of TS2 is shorter than that of $Cr(C_2H_2)$ and $CrCCH_2$. The migrating hydrogen atom is slightly closer to the C atom connecting with Cr than the other C atom. This transition state is very similar to that proposed previously by Silvestre and Hoffmann[37] for the intramolecular tautomerization between alkyne and vinylidene complexes but is quite different from the transition state for the reaction between $F_4W(C_2H_2)$ and F_4WCCH_2 reported by Stegmann and Frenking.[36]

The transition state TS2 is 40.5 kcal/mol higher in energy than the separated reactants: $Cr\ (^7P) + C_2H_2\ (^1\Sigma_g^+)$. The energy barrier for the $Cr(C_2H_2) \rightarrow CrCCH_2$ reaction is calculated to be 52.3 kcal/mol, which is significantly higher than the energy barrier for reaction 2 (30.9 kcal/mol). The photochemical process is controlled by the energy barrier existing in the system. Although HCrCCH and $CrCCH_2$ are very close in energy, the formation of $CrCCH_2$ is unfavorable due to the higher energy barrier.

Conclusions

Matrix isolation infrared absorption spectroscopic studies indicated that the ground-state chromium atoms reacted with acetylene in solid argon to form the $Cr(C_2H_2)$ molecules spontaneously on annealing. The $Cr(C_2H_2)$ molecule has a very low C−C stretching vibrational frequency of 1476.4 cm^{-1}. Density functional calculations showed that $Cr(C_2H_2)$ should not be considered as a chromium−acetylene π complex but rather as a metallocyclopropene. The $Cr(C_2H_2)$ molecule underwent photochemical rearrangement to the alkynyl hydride HCrCCH molecule upon ultraviolet−visible irradiation. This isomerization reaction was predicted to be slightly endothermic and proceeded via a transition state with an energy barrier of 30.9 kcal/mol. Although the vinylidene $CrCCH_2$ isomer was predicted to be slightly less stable than the $Cr(C_2H_2)$ and HCrCCH molecules, it was not observed in present experiments. DFT calculations predicted that the reaction from $Cr(C_2H_2)$ to $CrCCH_2$ proceeded via a transition state with an energy barrier of 52.3 kcal/mol, significantly higher than that of the $Cr(C_2H_2) \rightarrow HCrCCH$ reaction.

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