Dehalogenation of 1,1,2-Trichloro-1-fluoroethane over α-Cr$_2$O$_3$ (10$\bar{1}$2)

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The reaction of CFCl$_2$CH$_2$Cl over the stoichiometric Cr$_2$O$_3$ (10$\bar{1}$2) surface yields CFCl=CH$_2$, HC≡CH, and surface halogen. The 1,2-dihalo-elimination reaction to CFCl=CH$_2$ is initiated via C−Cl bond cleavage at the CFCl$_2$-end of the molecule to give a −CFClCH$_2$Cl haloalkyl surface intermediate. A rate-limiting β-chlorine elimination from the surface alkyl gives rise to the CFCl=CH$_2$ product. Acetylene is formed by the subsequent reaction of CFCl=CH$_2$ in series. The chlorine liberated from CFCl$_2$CH$_2$Cl binds at the five-coordinate surface Cr^{3+} sites on the stoichiometric surface and shuts down the dehalogenation chemistry by site blocking. No carbon buildup is observed on deactivated surfaces, and no evidence is seen for the replacement of surface lattice oxygen by halogen under the conditions of this study. At elevated temperatures, the thermal removal of surface chlorine is observed, and it is attributed to migration into the sample bulk.

I. Introduction

The reactions of halogen-substituted alkanes with chromia have been much studied because of their relevance to the vapor-phase manufacture of hydrofluorocarbon compounds (environmentally friendly refrigerants with low ozone-depleting potential) and because of interest in the destruction and conversion of chlorine-containing hydrochlorofluorocarbon (HCFC) analogues.[1−3] Typically, these reactions are conducted in the presence of HF where fluorination (for example, fluorine-for-chlorine exchange) is an expected result. The halocarbon reactions most commonly reported over Cr$_2$O$_3$ are summarized in Table 1.

Rowley, Webb, Winfield, and co-workers[4−7] have studied the interaction of halogenated compounds with Cr$_2$O$_3$ microcrystalline powders using radiolabeled HF, HCl, and halocarbon compounds. They unambiguously demonstrated the uptake of halogen by Cr$_2$O$_3$ during the initial "activation" phase of reaction, and found that ^{36}Cl and ^{18}F could be deposited on both untreated and pre-halogenated Cr$_2$O$_3$ catalysts by exposure to HX (X = halogen) or halocarbon compounds at 623 K. It was also reported that Cl and F are capable of replacing one another on the surface, and that halogen exchange occurs between the surface and various CFC compounds.[4,6,7] Direct halogen exchange with surface (HF)$_n$−HX oligomers was also proposed.[4,6] The resulting halogen exchange sequences yield a mix of halocarbon compounds over both untreated and pretreated (halogenated) Cr$_2$O$_3$ catalyst.

In studies of the trichlorotrifluoroethane/Cr$_2$O$_3$ system, Blanchard and co-workers focused on the disproportionation and isomerization of CFCl$_2$CF$_2$Cl to CCl$_3$CF$_3$ over Cr$_2$O$_3$ powder, supported Cr$_2$O$_3$, and AlF$_3$.[8−10] They found that disproportionation and isomerization reactions dominate over Cr$_2$O$_3$ in the absence of HF. They also observed that pretreating the surface with pyridine, a Lewis base, inhibits surface activity, indicating that Lewis acid sites (cation centers) are important to the reaction mechanism.[8] The presence of small amounts of the unsaturated compounds CCl$_2$=CCl$_2$ and CFCl=CCl$_2$ were also reported in the product mix.

TABLE 1: Halocarbon Reactions Reported To Occur over Cr$_2$O$_3$

Observed Reactions	Reaction Conditions
HF addition to C=C double bond	Dominant reaction in the presence of HF
Halogen exchange	Replacement of Cl by F is usually the desired reaction and is favored in the presence of HF.
Dehydrohalogenation (HF and HCl elimination)	Reaction may occur in the presence and absence of HF.
Disproportionation (dismutation)	Presence of HF not required.
Isomerization	Presence of HF not required.

Later work from Blanchard and co-workers focused a broader spectrum of halocarbon surface reactions including disproportionation, isomerization, dehalogenation, dehydrohalogenation, and halogen exchange.[11] They reported that halogen exchange dominates in the presence of HF, but that disproportionation, isomerization, and dehydrochlorination occurs without HF. It was suggested that fluorination, in the presence of HF, was governed by the acidity of the catalyst,[11] and that the catalytic activity for the fluorination of CF$_3$CH$_2$Cl to CF$_3$CH$_2$F is a function of the number of reversibly oxidizable chromium sites on the catalyst surface.[12,13] XPS measurements of fluorine uptake by the catalyst following exposures to HF and CF$_3$CH$_2$Cl yielded a maximum F/Cr ratio of 0.36, regardless of the treatment gas used.[13]

Other authors have postulated that the oxidation state of surface ions plays a crucial role in determining activity. On the basis of product distributions and thermal desorption data, Coulson et al.[14] propose that the reduction of high-valent chromium ions to Cr^{3+} is necessary to create active sites for the disproportionation of CHF$_2$Cl over powdered Cr$_2$O$_3$ microcrystalline catalyst. They argue that the active site is a coordinately unsaturated Cr−X center, which acts as a strong Lewis acid. Following exposures at 773 K, Coulson and co-workers[14] report XPS atomic percentages that correspond to F/Cr ratios of 0.22 and 0.30 for CHF$_3$ and HF, respectively.

Kohne and Kemnitz have studied the reactions of several halocarbons with chromia, and provided evidence that both direct halogen exchange and HX abstraction/addition reactions

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occur over fluorinated Cr_2O_3 catalyst in the presence of HF at 573 K.[15] Significant amounts of unsaturated haloalkenes were also found in the product mix, even in the presence of HF. Kohne and Kemnitz[15] argue that isomerization and disproportionation reactions may be disregarded, with or without HF present in the reaction mix, and that the product mix observed is the result of a sequence of reactions: (1) dehydrohalogenation (HX abstraction) of haloalkanes to olefins, (2) hydrohalogenation (Markovnikov HX addition) of olefins to haloalkanes, and (3) direct halogen exchange between haloalkanes and surface X.

Kemnitz and Niedersen[16] have also studied the isomerization reaction of CHF_2CHF_2 to CF_3CH_2F (HCFC-134a) over fluorinated Cr_2O_3, without HF. They propose that isomerization reactions occur in two steps. From deuterium labeling experiments, it was concluded that if chlorine could be excluded from the reacting system, then the isomerization reaction proceeds through HF elimination and subsequent HF addition by the Markovnikov rule. The presence of HCl or any chlorine-containing halocarbons was found to give rise to a "complex set of side reactions".[16]

Niedersen et al.[17] propose that Lewis acid sites are responsible for the CHF_2CHF_2 to CF_3CH_2F isomerization activity of Cr_2O_3. They used IR and UV−Vis spectroscopy of adsorbed CO and NH_3 to argue that Lewis acid sites are responsible for the isomerization. Using IR of adsorbed CO as a probe of the valence states and coordination numbers of surface chromium cations for various surface preparations, they report that five-coordinate Cr^{3+} is predominant on a fresh Cr_2O_3 catalyst, and that fluorination creates active isomerization sites by formation of CrF_3, which increases the Lewis acidity of the cation.

Changes to Cr_2O_3 that result from "activation" and fluorination were studied by Kemnitz and co-workers[18] using XPS and X-ray-excited AES to compare catalyst samples to Cr- and Al-fluoride standards. They argued that pretreatment of Cr_2O_3 by either HX or halocarbons causes the formation of α- and β-CrX_3 phases, and the nature of these sites was determined to be independent of the halogen source, in agreement with the work of Rowley et al.[4] Kemnitz et al. postulated that coordinately unsaturated (Lewis acid) Cr^{3+} ions exposed in the β-CrF_3 structure are responsible for the catalytic activity because of their Lewis acidity. They also proposed that all surface activation (i.e., halogen deposition) reactions occur via HX elimination, and that over a clean surface, halocarbon compounds decompose to CO_2, HF, and HCl, which in turn halogenate the surface.[18] The total halogen uptake (Cl and F) by the surface shows only a small variation, $0.44 \geq X/Cr \geq 0.27$, with pretreatment gas.[18]

The literature on Cr_2O_3 contains many suggestions concerning the reason for the eventual deactivation of the catalyst toward fluorination reactions. However, a clear picture of Cr_2O_3 deactivation has not emerged. Coke formation caused by the degradation of various HCFC compounds is often reported as the cause of surface deactivation.[3] Niedersen et al.[17] reported that surface coke may be burned off in the presence of O_2 at 673 K. The formation of halocarbon oligomers and structural changes to the surface have also been cited as mechanisms for surface deactivation.[10,18] Changes to the oxidation state of surface cations have also been suggested as a cause for surface deactivation.[10,14]

In the current study, the reaction of $CFCl_2CH_2Cl$ has been investigated over the α-Cr_2O_3 (10$\bar{1}$2) surface. $CFCl_2CH_2Cl$ (HCFC-131a) is an intermediate in the reaction pathway from trichloroethene to CF_3CH_2F (HCFC-134a) over chromia in the presence of HF.[3] The intent of this study is to investigate the reaction of this intermediate over a well-defined α-Cr_2O_3 (10$\bar{1}$2)
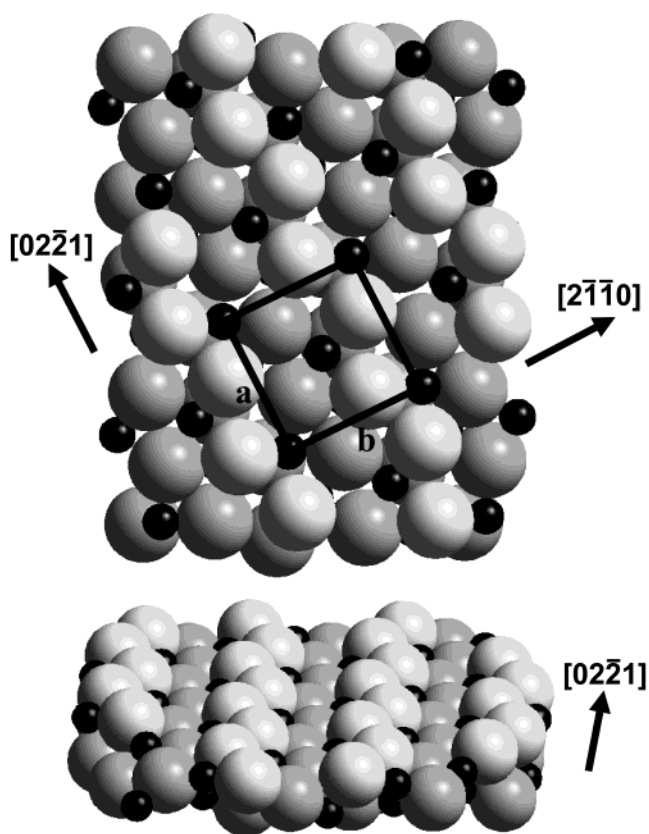

Figure 1. Ball model representation of the Cr_2O_3 (10$\bar{1}$2) surface. The top view shows the (10$\bar{1}$2) surface parallel to the plane of the page. A surface unit cell is drawn to show the periodicity. The bottom illustration shows a side view of one stoichiometric repeating layer. The smaller black spheres represent the chromium cations, and the oxygen anions are represented by the larger gray spheres.

surface with the intent of understanding the reaction chemistry in the absence of HF.

II. α-Cr_2O_3 (10$\bar{1}$2)

The α-Cr_2O_3 (10$\bar{1}$2) surface has been characterized in previous work.[19] The ideal, stoichiometric surface has only one local coordination environment for the surface cations and anions. A ball model representation of the ideal, stoichiometric surface is shown in Figure 1. The topmost atomic layer of the ideal surface is composed entirely of oxygen anions. The surface is nonpolar, and one full stoichiometric repeating unit normal to the surface contains five atomic layers arranged as [O, Cr, O, Cr, O]. The surface has a rectangular (almost square) periodicity with a ratio of sides of $a/b = 0.94$. At the ideal (10$\bar{1}$2) surface, all O^{2-} anions in the top atomic layer are three-coordinate with a pyramidal local coordination, and the Cr^{3+} cations in the second atomic layer are five-coordinate. Both ions have one degree of coordinative unsaturation relative to their bulk counterparts.[20] All ions below the top two atomic layers are fully coordinated. A nearly stoichiometric surface can be prepared by Ar^+ ion bombardment and annealing in a vacuum at 900 K.[19]

III. Experimental Methods

The reaction of $CFCl_2CH_2Cl$ over a nearly stoichiometric, (1×1), Cr_2O_3 (10$\bar{1}$2) surface was investigated using thermal desorption spectroscopy (TDS), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). Experiments were conducted in an ion-pumped UHV chamber

equipped with a Physical Electronics Model 15-155 single-pass CMA for AES, an Inficon Quadrex 200 mass spectrometer for TDS and a set of Vacuum Generators 3-grid reverse view LEED optics. A broad beam ion gun was used for sample cleaning. The base operating pressure for this study was 1×10^{-10} Torr.

AES data were collected using an incident electron beam of 5 keV for all measurements. Spectra were collected in N(E) mode and differentiated numerically. All AES measurements were conducted at 800 K to avoid sample charging. Because of overlap between the primary oxygen and chromium Auger peaks, the surface chromium concentration was followed by measuring the Cr $L_{2,3}M_{2,3}M_{2,3}$ (490 eV) peak-to-peak height.[19] Atomic Cl/Cr ratios were estimated with AES using appropriate sensitivity factors for the Cl KLL signal[21] and the Cr $L_{2,3}M_{2,3}M_{2,3}$ signal.[19] Electron stimulated reduction of the surface (i.e., lattice oxygen removal) was not observed during AES experiments.

The α-Cr_2O_3 crystal was oriented to within $1°$ of the ($10\bar{1}2$) surface using Laue back-reflection and polished to a final mirror finish with 0.25 μm diamond paste. The sample was mechanically clamped onto a tantalum stage that was fastened to LN_2-cooled copper electrical conductors. A Type K thermocouple was attached through a hole in the stage to the back of the single crystal using Aremco #569 ceramic cement. This arrangement allowed direct measurement of the sample temperature. A nearly stoichiometric, (1×1) surface was prepared by ion-bombardment, followed by annealing to 900 K.[19]

1,1,2-Trichloro-1-fluoroethane ($CFCl_2CH_2Cl$) (97% min) (PCR, Inc.) was used as received. Gas dosing was accomplished by backfilling the chamber through a variable leak valve. All doses for $CFCl_2CH_2Cl$ TDS experiments were conducted at 163 K. The reported dose sizes have been corrected for ion gauge sensitivity,[22] and all desorption traces and quantities have been corrected for mass spectrometer sensitivity.[22-25]

IV. Results

A combination of thermal desorption and AES results reveals that $CFCl_2CH_2Cl$ decomposes into $CFCl{=}CH_{2(g)}$ (HCFC-1131a), acetylene ($HC{\equiv}CH_{(g)}$), and adsorbed halogen. Gas-phase products were identified by comparison of mass spectrometer cracking patterns to thermal desorption peak intensities. The relative intensities of four m/z signals were used to identify both $CFCl{=}CH_2$ (80, 45, 26, 31) and acetylene (26, 25, 27, 13). Other products were excluded by a search that included m/z values ranging from 2 to 200. Specifically, no CO, CO_2, HCl, HF, Cl_2, F_2, chloroacetylene, fluoroacetylene, or chromium halide gas-phase reaction products were observed during TDS. No surface carbon was detected with AES following $CFCl_2$-CH_2Cl decomposition; only surface halogen was observed.

1. $CFCl_2CH_2Cl$ Thermal Desorption. Figure 2 shows representative desorption traces for the reactant and gas-phase products following the second dose of $CFCl_2CH_2Cl$ in a TDS series of consecutive 0.03 L doses started on a clean, nearly stoichiometric ($10\bar{1}2$) surface. Nearly 100% of the $CFCl_2CH_2$-Cl reactant is converted to products during initial TDS runs, as evidenced by the small desorption peak for the reactant molecule (solid line). The principal product observed is the haloethene $CFCl{=}CH_2$ (dashed line), formed by a net 1,2-dihalo-elimination reaction from $CFCl_2CH_2Cl$. The $CFCl{=}CH_2$ product desorption temperature is similar to the desorption temperature for the $CFCl_2CH_2Cl$ reactant, suggesting a rate-limiting surface reaction involving a common surface intermediate for these two desorbing species (see below). Acetylene (dotted line) is also formed when the total exposure is low, and yields two desorption features, one near 335 K and another near 480 K. The acetylene
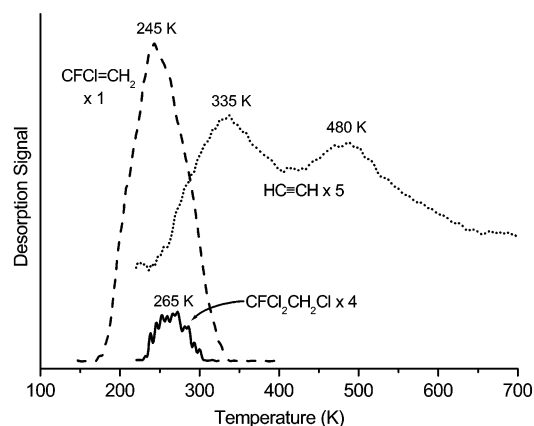

Figure 2. Desorption features observed following the second 0.03 L dose of $CFCl_2CH_2Cl$ in a TDS series initiated on a clean, (1×1), nearly stoichiometric surface. $CFCl_2CH_2Cl$ (solid line), $CFCl{=}CH_2$ (dashed line), acetylene (dotted line). The baseline for acetylene has been offset for clarity.
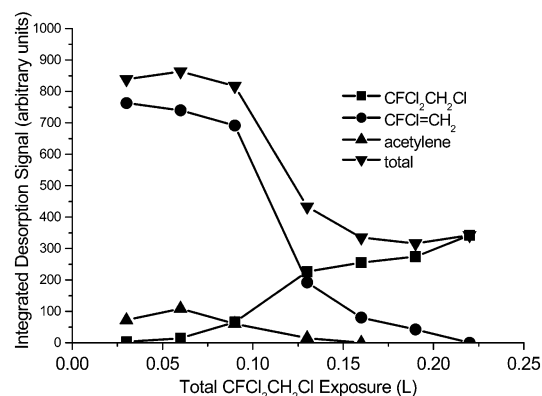

Figure 3. The relative quantities desorbed for $CFCl_2CH_2Cl$ and reaction products. The TDS experiment consisted of sequential 0.03 L doses starting on a clean, (1×1), nearly stoichiometric Cr_2O_3 ($10\bar{1}2$) surface. The sum total for all desorbing species (reactant and products) is also shown.

desorption trace from $CFCl_2CH_2Cl$ decomposition is identical to the trace obtained directly from the reaction of $CFCl{=}CH_2$ over Cr_2O_3 ($10\bar{1}2$) in thermal desorption experiments.[26]

Initially, the nearly stoichiometric Cr_2O_3 ($10\bar{1}2$) surface is very reactive toward $CFCl_2CH_2Cl$, converting nearly 100% of the reactant to products. Figure 3 shows the relative amounts of reactant and products desorbed from the surface during a series of consecutive 0.03 L doses of $CFCl_2CH_2Cl$ initiated on a clean, nearly stoichiometric surface. The ratios of $CFCl_2CH_2$-Cl to $CFCl{=}CH_2$ to $HC{\equiv}CH$ in the desorbing gases from an initial 0.03 L TDS run is 1:512:40. The amount of the $CFCl_2$-CH_2Cl reactant desorbed from the surface is small following the first two doses, but increases significantly following 0.10 L of total $CFCl_2CH_2Cl$ exposure. The high reactivity of $CFCl_2$-CH_2Cl over clean Cr_2O_3 ($10\bar{1}2$) is evidenced by the small desorption signal intensity of the reactant molecule during initial TDS runs.

As shown in Figure 3, the quantity of $CFCl{=}CH_2$ and acetylene products remains relatively constant for the first three 0.03 L doses of $CFClCH_2Cl$, then the amount of each rapidly declines. Acetylene production ceases at around 0.15 L of total exposure, and $CFCl{=}CH_2$ production continues until a total $CFCl_2CH_2Cl$ exposure of around 0.22 L is reached. The decline in product quantities indicates that the surface becomes deactivated toward $CFCl_2CH_2Cl$ decomposition by a total exposure of 0.25 L. The sum of all desorbing species decreases by
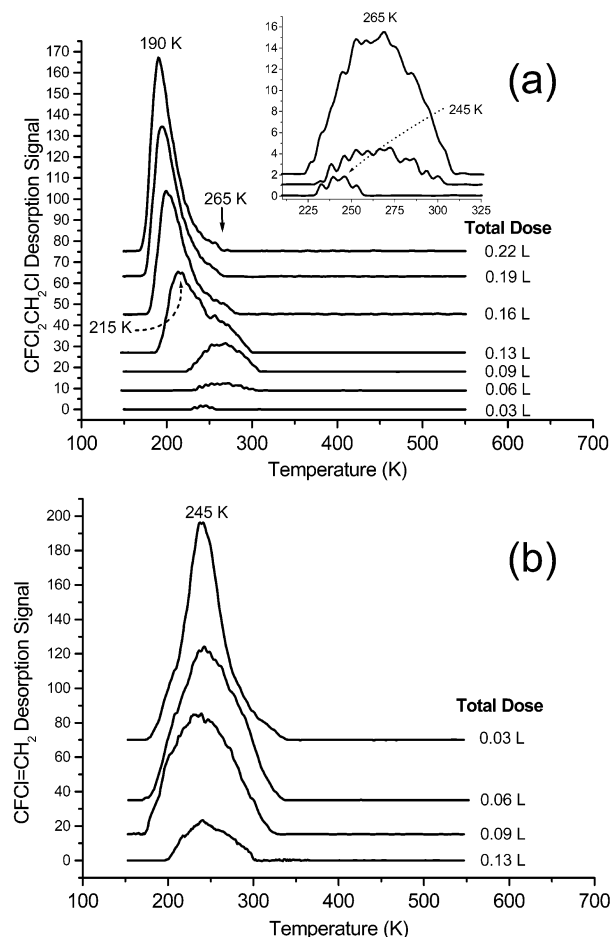
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Figure 4. Desorption traces of $CFCl_2CH_2Cl$ reactant (a) and $CFCl= CH_2$ product (b) for a series of consecutive 0.03 L doses initiated on a clean, (1×1), nearly stoichiometric surface. The baselines of the desorption traces have been offset for clarity. The inset in (a) shows the traces for the first three doses at greater magnification.

Figure 5. AES spectrum of a Cr_2O_3 ($10\bar{1}2$) surface deactivated by repeated exposure to and thermal desorption of $CFCl_2CH_2Cl$. The AES Cl/Cr ratio for the spectrum is 0.32.

approximately 50% as the surface becomes deactivated, indicating a decrease in the $CFCl_2CH_2Cl$ sticking coefficient as the surface chemistry shuts down. AES data presented below demonstrate that the surface Cl/Cr ratio increases as the amount of products detected in TDS declines. This observation suggests that deposition of halogen onto the sample surface is responsible for the observed deactivation.

Figure 4a shows desorption traces of the dosed molecule, $CFCl_2CH_2Cl$, for the same series of consecutive 0.03 L doses described in Figure 3. Two features are apparent in the desorption traces of the reactant molecule: a high-temperature feature near 265 K and a lower temperature feature around 190−215 K. The high-temperature contribution occurs at low total exposures and initially has a peak desorption temperature of 245 K (see insert in Figure 4a). The high-temperature feature increases in intensity and shifts to 265 K during the first three 0.03 L doses. Following the fourth dose, a low-temperature contribution to the $CFCl_2CH_2Cl$ desorption feature is observed around 215 K, while the high-temperature peak remains relatively unchanged. In subsequent TDS runs, the high-temperature feature rapidly dies out while the low-temperature feature increases in intensity and shifts downward to around 190 K. Differences in the peak desorption temperatures and the shapes of the two $CFCl_2CH_2Cl$ desorption features suggest that two separate desorption processes occur for the reactant molecule.
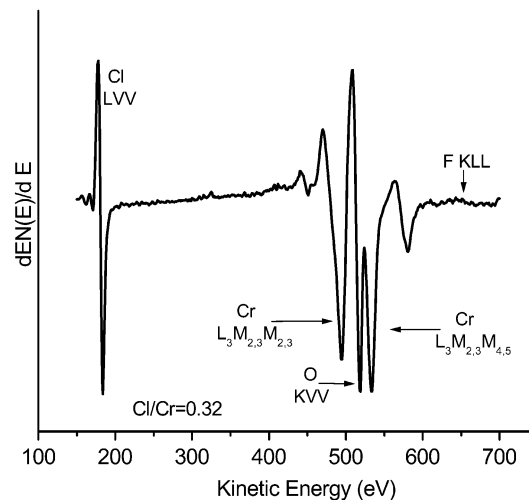
Figure 4b shows desorption traces for the product $CFCl= CH_2$ formed during the same series of 0.03 L doses. The $CFCl= CH_2$ desorption peak initially occurs around 245 K and broadens to higher temperatures coincident with the shift of the high-temperature (245−265 K) $CFCl_2CH_2Cl$ desorption feature in Figure 4a prior to surface deactivation. A decrease in the amount of product $CFCl=CH_2$ is observed around 0.13 L as the 1,2-dihalo-elimination reaction of $CFCl_2CH_2Cl$ to $CFCl=CH_2$ shuts down. The decrease in product $CFCl=CH_2$ occurs in tandem with the increase in reactant ($CFCl_2CH_2Cl$) desorption in the lower temperature range (190−215 K) described above. The similar temperature ranges for the product $CFCl=CH_2$ desorption and the high-temperature desorption feature of the $CFCl_2$-CH_2Cl reactant suggest that these desorbing species originate from a common surface intermediate and share the same rate-limiting surface reaction step.

2. HC≡CH Product. Dosing $CFCl_2CH_2Cl$ onto stoichiometric Cr_2O_3 ($10\bar{1}2$) yields an acetylene TDS spectrum containing two features, one around 335 K and the other around 480 K as shown in Figure 2. Acetylene desorption traces obtained from $CFCl_2CH_2Cl$ decomposition over a nearly stoichiometric surface are essentially identical in both shape and peak temperature to the acetylene formed directly from $CFCl=CH_2$ decomposition on a nearly stoichiometric surface.[26] However, the quantity of acetylene made from $CFCl_2CH_2Cl$ decomposition is small compared to product $CFCl=CH_2$, representing less than 10% of the total products prior to surface deactivation.

3. Deposition of Halogen. AES of the sample surface following the reaction of $CFCl_2CH_2Cl$ reveals a significant buildup of surface chlorine. The presence of product acetylene indicates that a small amount of surface fluorine should also be seen, but fluorine is not readily seen on this surface using AES because of a very rapid electron stimulated loss from the surface.[26] The rate of surface chlorine loss is, however, sufficiently slow to allow for quantification. Figure 5 shows the AES spectrum of a Cr_2O_3 ($10\bar{1}2$) surface that has been deactivated by $CFCl_2CH_2Cl$ exposure and reaction. The spectrum was collected at 800 K to avoid sample charging, and gives an AES Cl/Cr ratio of 0.32 ± 0.01. No carbon is observed on the deactivated surface, and no evidence is seen for the replacement of lattice oxygen by halogen for these thermal desorption conditions.

Figure 6 shows a comparison of the variation in surface AES Cl/Cr ratio (left axis) and the sum of the amounts of product
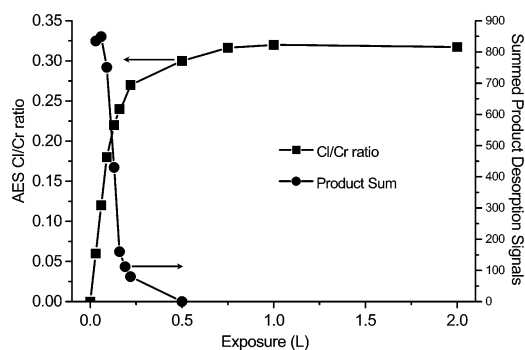
Figure 6. The total quantity of products (sum of CClFCH$_2$ and HC≡CH) and variation in surface Cl/Cr ratio for a series of consecutive 0.03 L doses of CFCl$_2$CH$_2$Cl initiated on a clean, (1 × 1), nearly stoichiometric surface.

(CFCl=CH$_2$ and HC≡CH) desorbed in TDS (right axis) for a series of consecutive 0.03 L doses of CFCl$_2$CH$_2$Cl initiated on a clean, nearly stoichiometric Cr$_2$O$_3$ (10$\bar{1}$2) surface. AES spectra were collected immediately following each TDS run. The surface Cl/Cr ratio rises rapidly then levels off after a total exposure of around 0.75 L. The surface Cl/Cr ratio increases most rapidly for total CFCl$_2$CH$_2$Cl exposures below 0.25 L, when the conversion to products is highest. As less product is made, the product sum declines while the surface Cl/Cr ratio levels off at about 0.32, indicating that surface halogen is deposited as a result of CFCl$_2$CH$_2$Cl decomposition. The surface Cl/Cr ratio stops increasing when the product formation ceases.

LEED was used to examine the changes in surface periodicity with chlorine deposition. The clean, nearly stoichiometric surface exhibits a (1 × 1) periodicity.[19] As chlorine builds up on the surface, an increase in diffuse background is observed at low chlorine coverages, but no change is seen in the underlying (1 × 1) periodicity. As the coverage approaches saturation, the (1 × 1) LEED pattern sharpens and the diffuse background decreases. The variation in the LEED pattern suggests that the chlorine adlayer is disordered at low coverage, but approaches an integer Cl coverage per surface unit cell at saturation.

Due to molecular stoichiometry and the product distribution, the halogen deposited onto the Cr$_2$O$_3$ (10$\bar{1}$2) surface from CFCl$_2$-CH$_2$Cl decomposition should be overwhelmingly chlorine. On the basis of the relative quantities of CFCl$_2$CH$_2$Cl and HC≡CH formed, the expected amount of surface fluorine is estimated to be only about 4% of the total amount of deposited surface halogen. While the surface fluorine cannot be quantified with AES because of its rapid electron-stimulated removal, disregarding the presence of fluorine at the halogen-saturated surface should introduce an approximate error of only about 0.01 in the value of X/Cr. Therefore, the AES Cl/Cr ratio of 0.32 may be regarded as an excellent approximation to the total halogen content (X/Cr) of the halogen-saturated (deactivated) surface.

A surface deactivated by CFCl$_2$CH$_2$Cl thermal desorption treatments yields an experimental AES Cl/Cr ratio of 0.32. Using an exponential AES signal decay model, an estimate was made of the expected Cl/Cr ratio for a surface containing one adsorbed chlorine adatom per five-coordinate surface cation. The calculation involves conventional layer-by-layer summations assuming an exponential signal decay with increasing sampling depth, and ignoring diffraction effects. Interlayer spacings in the substrate were assumed to be the same as in bulk α-Cr$_2$O$_3$. An electron mean free path of 9 Å was estimated from the "universal curve"[27] and was used to describe the Auger emission for both Cr and O lines, which occur at similar kinetic energies. On the

basis of the (1 × 1) LEED pattern observed for a chlorinated surface, it was assumed that the chlorine adatoms are located on the surface cations in approximate registry with the positions of the missing nearest-neighbor oxide anions that would be found in the bulk structure. A Cr−Cl bond length was estimated using the combined ionic radii for chromium(III) (0.63 Å) and chloride ion (1.32 Å) obtained from the literature.[28] For a sample orientation normal to the axis of the CMA and a signal collection geometry 42° off the spectrometer axis, the expected Cl/Cr ratio for 100% coverage of surface cations by chlorine is estimated to be 0.325. This value is in good agreement with the Cl/Cr = 0.32 measured from a halogen-saturated (deactivated) surface. Therefore, the deactivated (Cl/Cr = 0.32) surface may be considered to have a chlorine coverage of essentially one adsorbed chlorine adatom per surface Cr^{3+} cation. Additional thermal desorption runs following adsorption at 163 K produce no increase in the Cl/Cr ratio of 0.32 and no additional product. In addition, CFCl$_2$CH$_2$Cl exposures of up to 2.0 L at 773 K produced no increase in the AES Cl/Cr ratio beyond Cl/Cr = 0.32. Deactivation of the Cr$_2$O$_3$ (10$\bar{1}$2) surface toward CFCl$_2$-CH$_2$Cl decomposition in the thermal desorption experiments is directly attributed to site blocking of surface cations by deposited halogen adatoms.

4. Thermal Loss of Surface Chlorine. It was found that chlorine can be removed from the sample surface by heating to 1100 K. AES spectra of a deactivated surface (AES Cl/Cr = 0.32) taken following five minutes of heating at 1100 K show that all of the Cl is removed, and the nearly stoichiometric surface is returned. The desorption of halogen and halogen-containing species was checked for with TDS, and no desorbing halogen or halogen-containing products other than CFCl=CH$_2$ were detected. The lack of evidence for desorption of surface halogen or halogen-containing species (ex., CrX$_n$) suggests that the thermal removal of chlorine from the sample surface occurs via migration into the sample bulk.

AES experiments were conducted on deactivated surfaces prepared by exposure to CFCl$_2$CH$_2$Cl to determine the rate of Cl thermal migration. AES spectra were collected as a function of time to monitor the loss of chlorine for three different annealing temperatures. The variation in Cl/Cr ratio with time is shown in Figure 7a. The time dependence of the surface Cl/Cr ratio is reasonably fit by first-order kinetics at each temperature. An Arrhenius analysis (Figure 7b) yields a first-order activation energy for chlorine migration of 173 kJ/mol.

Given the rapid electron stimulated loss of fluorine, the kinetics of thermal fluorine removal from the surface cannot be directly addressed with AES measurements, although the deposition of a small amount of fluorine is indicated by the stoichiometry of CFCl$_2$CH$_2$Cl decomposition to acetylene. However, since no additional fluorinated desorption products other than CFCl=CH$_2$ were observed, it seems reasonable to expect that any thermal loss of fluorine from the surface would occur via migration into the sample bulk, as suspected for chlorine.

V. Discussion

The decomposition of CFCl$_2$CH$_2$Cl over nearly stoichiometric Cr$_2$O$_3$ (10$\bar{1}$2) yields surface halogen and CFCl=CH$_2$ as major products, and acetylene as a minor product. As mentioned above, acetylene is the only gas-phase product observed for the reaction of CFCl=CH$_2$ over this same surface.[26] Given that the desorption traces for acetylene from both starting reactants (CFCl$_2$-CH$_2$Cl and CFCl=CH$_2$) are essentially identical, the decomposition pathway for CFCl$_2$CH$_2$Cl over the Cr$_2$O$_3$ (10$\bar{1}$2) is

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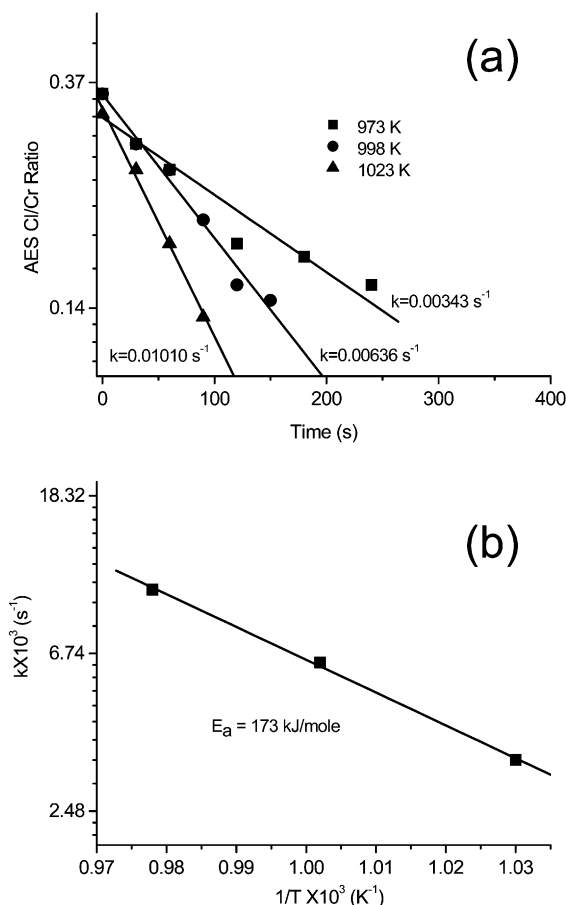*J. Phys. Chem. B, Vol. 107, No. 22, 2003* **5187**

Figure 7. Kinetics of thermal Cl loss from the Cr_2O_3 ($10\bar{1}2$) surface: (a) first-order analysis for the rate constant, k, at several temperatures, and (b) Arrhenius analysis for determination of the activation energy.

attributed to two reactions in series with acetylene formed by the further reaction of product $CFCl=CH_2$:

$$CFCl_2CH_2Cl \rightarrow CFCl=CH_2 + 2Cl_{(s)}$$

$$CFCl=CH_2 \rightarrow HC\equiv CH + Cl_{(s)} + F_{(s)}$$
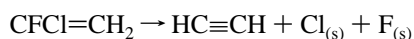
While HX abstraction is one of the most often reported reactions for $CFCl_2CH_2Cl$ and similar HCFC compounds over Cr_2O_3 powders,[13,15,29] no dehydrohalogenation reaction products are observed under the conditions of this thermal desorption study. The reaction of $CFCl_2CH_2Cl$ to $CFCl=CH_2$ most closely resembles the Zn-based chemistry utilized in organic synthesis for the dehalogenation of vicinal dihalides to alkenes.[30]

1. $CFCl_2CH_2Cl$ Adsorption/Desorption and Reaction Pathway to $CFCl=CH_2$. A. 210−190 K $CFCl_2CH_2Cl$ Desorption Channel. The low-temperature (210−190 K) $CFCl_2CH_2Cl$ desorption channel is first observed after some initial halogenation of the surface as the formation of reaction products declines. The low peak temperature suggests that desorption of a molecularly bound $CFCl_2CH_2Cl$ surface species is responsible for this desorption feature. The activation energy for desorption from this state (190 K) is estimated to be around 48 kJ/mol using the Redhead equation and a normal, first-order pre-exponential factor of 10^{13} s^{-1}.[31]

It is significant that the low-temperature $CFCl_2CH_2Cl$ desorption feature is not observed during initial TDS runs at small doses. AES spectra of the surface taken in conjunction with TDS experiments show that this feature grows in as the surface becomes progressively halogenated, suggesting that the low-

temperature desorption state is the result of surface halogenation associated with the deactivation of the surface under the conditions of this thermal desorption study. Since molecular adsorption and desorption of $CFCl_2CH_2Cl$ is observed on the deactivated surface after the halogenation (site blocking) of essentially all the surface Cr^{3+} cation sites, desorption via the low-temperature channel is thought to originate from molecular $CFCl_2CH_2Cl$ bound at chlorinated cation sites or three-coordinate oxygen anions via a weak physical interaction. The total uptake ($CFCl_2CH_2Cl$ plus products) decreases by about 50% as the surface changes from a clean, stoichiometric condition to chlorine-saturated (deactivated).

B. 265 K Reaction Channel. Despite the high conversion to products on a clean surface, a small $CFCl_2CH_2Cl$ desorption feature is observed (245−265 K) in the same temperature range as product $CFCl=CH_2$ during initial 0.03 L doses (Figure 4). The coincident desorption of both the $CFCl_2CH_2Cl$ reactant and $CFCl=CH_2$ product molecules in TDS indicates that they arise from a common surface intermediate and share the same rate-limiting step. Additionally, the desorption temperature observed for product $CFCl=CH_2$ (245 K and broadened to higher temperatures) from the reaction of $CFCl_2CH_2Cl$ is 30−50 K higher in temperature than the desorption signal observed for a molecular $CFCl=CH_2$ adsorbate.[26] The higher desorption temperature for product $CFCl=CH_2$ also indicates a reaction-limited process in this temperature range. An apparent first-order activation energy for this process of 69 kJ/mol can be estimated with the Redhead equation[31] assuming a normal first-order pre-exponential of 10^{13} s^{-1}.

The first step in the surface reaction mechanism is dissociative adsorption of $CFCl_2CH_2Cl$ via C−Cl bond cleavage at five-coordinate Cr^{3+} cations. The literature indicates that the C−Cl bond on the more chlorinated carbon ($CFCl_2-$ group) is the weakest bond, and hence the most likely bond to be broken during dissociative adsorption.[4,32−34] In support of this idea, we have found a pattern of decreasing reactivity with modification to this end group (**$CFCl_2CH_2Cl$** > **CF_2ClCH_2Cl** ≫ **CF_3CH_2-Cl**) due to an increasing barrier to dissociative adsorption on Cr_2O_3 ($10\bar{1}2$).[35] Since there is no change in composition of the $-CH_2Cl$ end group on the opposite end of the molecule for this sequence of reactants, these results are in agreement with the idea that the initial attack of the surface is at the C−Cl bond of the $CFCl_2-$ group in $CFCl_2CH_2Cl$. Similarly, Gellman and co-workers[33,34] studied the rate constant for dechlorination of a sequence of haloethanes over Pd(111), and found that the rate of dechlorination is reduced for haloethanes containing fewer chlorine atoms per carbon. They also found that the transition state for the dechlorination reaction is not highly polarized relative to the initial state, suggesting homolytic C−Cl bond cleavage. The reaction pathway in this study is attributed to the dissociative adsorption of $CFCl_2CH_2Cl$ which results in a surface alkyl group ($-CFClCH_2Cl$) and adsorbed chlorine, $Cl_{(s)}$, both bound at surface cation sites. Similar alkyl groups attached to transition metal cations are well-known in the organometallic literature, and a strong interaction between chlorine and microcrystalline Cr_2O_3 has been documented in the catalysis literature[1,35] and observed in this study.

Following the dissociative adsorption of $CFCl_2CH_2Cl$, two elementary reaction pathways are operable:

(1) The surface alkyl may undergo a rate-limiting β-chlorine elimination step to form the $CFCl=CH_2$ product molecule and a second $Cl_{(s)}$.

$$Cr-CFClCH_2Cl \rightarrow Cr-Cl + CFCl=CH_2$$
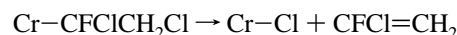
SCHEME 1: Reaction Pathway from CFCl₂CH₂Cl to CFCl=CH₂
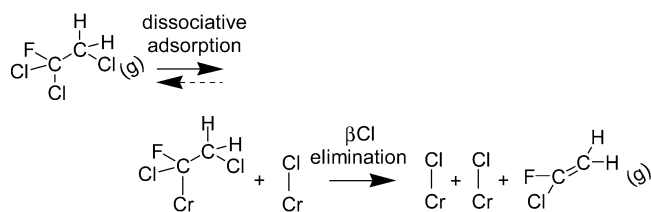
(2) The surface alkyl may recombine with chlorine liberated by the rate-limiting β elimination to reform the CFCl₂CH₂Cl reactant molecule.

$$Cr-CFClCH_2Cl + Cl_{(s)} \rightarrow Cr- + CFCl_2CH_2Cl_{(g)}$$
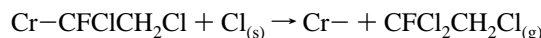
Chlorine is provided for the recombination reaction via the same rate-limiting β-chlorine elimination step, as evidenced by coincident desorption of CFCl=CH₂ and CFCl₂CH₂Cl near 265 K. Note that the desorption rate of CFCl₂CH₂Cl formed by recombination of Cl and surface alkyl should be rapid since the recombination process occurs above the molecular desorption temperature (210 K). The organometallic literature contains many examples of β-halogen elimination from alkyl complexes,[36−38] and β-halogen elimination has been observed from haloalkyl surface intermediates on Ag(111)[39] and Si(100).[40]

The first reaction to CFCl=CH₂ is favored initially, as evidenced in TDS by the much larger yield of CFCl=CH₂ compared to CFCl₂CH₂Cl at 265 K, but the probability for the recombination reaction increases (slightly) as the extent of surface chlorination increases, as evidenced by the increase in CFCl₂CH₂Cl desorption at high temperatures with the first few exposures. The combination of TDS and AES data demonstrates that as the surface becomes increasingly chlorinated, the recombination to CFCl₂CH₂Cl becomes increasingly favored. However, as the halogen content of the surface nears saturation, both pathways become unavailable as the dissociation of CFCl₂-CH₂Cl shuts down due to a lack of exposed (coordinately unsaturated) cations. It is postulated that the chlorine liberated via β-elimination bonds to five-coordinate Cr³⁺ sites when they are available (i.e., at low surface Cl/Cr ratios). As the surface becomes increasingly halogenated, bare cation sites become less available and recombination of chlorine with a surface alkyl becomes more likely, as evidenced by the increase in CFCl₂-CH₂Cl desorption. Consequently, the CFCl₂CH₂Cl desorption intensity increases and the product CFCl=CH₂ intensity decreases as the surface halogen content increases. Eventually, surface deactivation results in essentially 100% of surface cations being capped by adsorbed halogen and the formation of CFCl=CH₂ is completely suppressed. The reaction pathway from haloalkane to haloalkene is shown in Scheme 1.

2. Reaction Pathway to HC≡CH Product. The acetylene desorption traces observed during CFCl₂CH₂Cl thermal desorption are essentially identical to the traces observed for the direct reaction of CFCl=CH₂ to acetylene over this same surface.[26] Both CFCl₂CH₂Cl and CFCl=CH₂ reactants produce traces that contain two product acetylene desorption features, with similar peak shapes and peak desorption temperatures. The similarity in TDS characteristics demonstrates that the kinetics and surface species involved in both desorption processes are the same.

The second overall reaction step in the sequence to acetylene has been studied in detail.[26] CFCl=CH₂ undergoes C−Cl bond cleavage to form a surface fluorovinyl intermediate (Cr−CF= CH₂) followed by α-fluorine elimination to yield a surface vinylidene intermediate (Cr=C=CH₂). Isomerization of vi-

SCHEME 2: Reaction Pathway from CFCl=CH₂ to HC≡CH from Ref 26
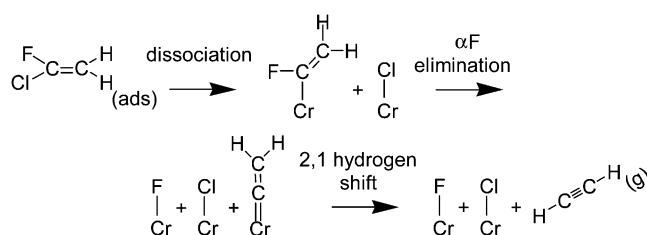
nylidene to acetylene then occurs via a 2,1 hydrogen shift.[26] The 335 K acetylene feature is desorption limited, and associated with the first-order desorption of molecularly bound HC≡CH, while the 480 K feature is reaction limited with first-order kinetics.[37,38] The reaction pathway from haloalkene to acetylene is shown in Scheme 2.

3. Surface Chlorine. Various authors have reported the uptake of halogen by Cr₂O₃ microcrystalline powder. Kemnitz et al.[18] used XPS to measure the amount of halogen uptake by microcrystalline Cr₂O₃ powder exposed to CFCl₂CH₂Cl at 673 K and atmospheric pressure. They reported a maximum X/Cr ratio of approximately 0.44. Blanchard and co-workers[8,10] studied the uptake of fluorine over microcrystalline Cr₂O₃ powder exposed to CF₃CH₂Cl at 653 K and atmospheric pressure and reported a F/Cr ratio of 0.36. Coulson and co-workers[14] report that exposures of CHF₃ and HF at 698 K over microcrystalline Cr₂O₃ yielded F/Cr ratios of 0.22 and 0.30, respectively. The AES Cl/Cr = 0.32 reported herein lies within the range of X/Cr values found in the catalysis literature.

Under the conditions of this thermal desorption study, the deactivation of the Cr₂O₃ (10$\bar{1}$2) surface was found to be coincident with a 1:1 surface chlorine-to-cation ratio (i.e., a halogen-saturated surface). Deactivation of the surface occurs by "capping" surface Cr³⁺ cations with chlorine (i.e., by site blocking), thereby preventing reaction by isolating the surface chromium cations from adsorbates. Site blocking by fluorine has similarly been reported in our studies of the reaction of CFCl=CH₂ to acetylene.[26] A similar argument was presented by Kemnitz et al.[18] to explain the deactivation of microcrystalline Cr₂O₃ powder samples toward fluorination reactions. No evidence was seen for the replacement of surface lattice oxygen by chlorine under the conditions of this study.

The absence of gas-phase desorption products during thermal treatments of the chlorine-saturated surface suggests that surface chlorine loss occurs via migration into the sample bulk. A similar result has been reported for fluorine.[26] While no reports of halogen migration into Cr₂O₃ could be found in the surface science literature, Freund and co-workers report that sodium adatoms on Cr₂O₃(0001) thin films also migrate into the sample bulk.[41]

4. Comparison to the Catalysis Literature. The chemistry observed in the thermal desorption experiments in this study differs significantly from the reported chemistry of haloalkanes over supported and powdered chromia catalysts. Dehalogenation chemistry is observed, but no dehydrohalogenation, halogen exchange, isomerization, or disproportionation chemistry is seen. The reaction pathway from haloalkane to haloalkene is the primary chemistry observed in this study, and occurs below room temperature between 245 and 265 K. In contrast, catalytic studies are typically conducted between 600 and 700 K.[4−9,11] It is likely that the typical catalytic reactions that were not observed have higher activation energies than the reaction and desorption steps observed in this study. Given the low activation

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barrier for desorption of $CFCl_2CH_2Cl$ from the halogenated surface, the reactant is desorbed at low temperature before the barrier to the unobserved reactions can be scaled. Under typical catalytic reaction conditions, the higher partial pressure of reactants will yield some stationary coverage of reactant at higher temperatures.

The deactivation of the surface due to site blocking of Cr^{3+} cations by chlorine adatoms also contrasts significantly with the catalytic literature on haloalkane reactions over chromia. The level of halogenation observed for the deactivated Cr_2O_3 $(10\bar{1}2)$ surface in this study $(Cl/Cr = 0.32)$ is similar to that reported for halogen-pretreated (i.e., activated) chromia catalysts. While it is not necessarily apparent that the majority of surface cations sites are capped (blocked) at these halogen coverages on chromia catalysts as they are on Cr_2O_3 $(10\bar{1}2)$, the elevated reaction temperatures in the catalytic studies may give rise to a higher level of reactivity of halogen adatoms. The surface-to-bulk diffusion of chlorine observed in this study indicates the mobility and likely higher reactivity of halogen adatoms at higher temperatures.

Despite the differences observed between this model thermal desorption study and the catalysis of chromia in HCFC reactions, the current results do add insight into possible elementary steps involved in the catalysis. The net 1,2-dihalo-elimination reaction (dissociation and β halogen elimination) is an additional pathway that may be operable in addition to dehydrohalogenation (H−X elimination) to give haloalkene from haloalkane. The apparent reversibility of the first elementary step in this reaction sequence (dissociative adsorption) with kinetics attributable to a β halogen rate-limiting step suggests a possible elementary reaction sequence associated with halogen exchange. The recombination step is only observed for partially halogenated surfaces, and represents an alternative to halogen trapping at coordinately unsaturated surface cations sites. Halogen exchange processes could occur by reaction of surface haloalkyl intermediates with mobile surface halogen species (for example, HX or halogen liberated by other processes such as β elimination on a halogenated surface) to reform haloalkane.

VI. Conclusions

$CFCl_2CH_2Cl$ has been found to decompose over a nearly stoichiometric Cr_2O_3 $(10\bar{1}2)$ surface to $CFCl{=}CH_2$, acetylene, and surface halogen. The chlorine removed from $CFCl_2CH_2Cl$ was found to bind strongly to the surface. Chlorine bound at five-coordinate surface Cr^{3+} sites shuts down the dehalogenation reactions by site blocking. At elevated temperatures, the thermal removal of surface chlorine is observed and attributed to migration into the sample bulk. The first-order activation energy for this chlorine diffusion process is 173 kJ/mol.

The reaction proceeds via dissociative adsorption of $CFCl_2$-CH_2Cl at the $CFCl_2-$ end of the molecule through a presumably homolytic C−Cl bond cleavage to give a haloalkyl, $-CFClCH_2$-Cl, surface intermediate. A rate-limiting β-chlorine elimination from the surface alkyl intermediate gives rise to the $CFCl{=}CH_2$ product. A small quantity of acetylene is also formed by the subsequent reaction of $CFCl{=}CH_2$ in series. No carbon buildup was observed on deactivated surfaces, and no evidence was seen for the replacement of surface lattice oxygen by halogen under the conditions of this study.

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(23) An ion gauge sensitivity of 5.9 was used for $CFCl{=}CH_2$ from the correlation in ref 25. A relative mass spectrometer sensitivity factor of 1.45 was determined experimentally for $m/z = 80$.

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