JOURNAL OF CATALYSIS 140, 103–120 (1993)

Chromium Oxide-Catalyzed Disproportionation of Chlorodifluoromethane: A Mechanism Study

D. R. COULSON, P. W. J. G. WIJNEN, J. J. LEROU, AND L. E. MANZER

Central Research & Development, Du Pont Company, P.O. Box 80262, Experimental Station, Wilmington, Delaware, 19880-0262

Received July 20, 1992; revised September 21, 1992

The facile disproportionation of CHF_2Cl over chrome(III) oxide-based catalysts has allowed the study of catalyst activation and disproportionation as separate processes. Using both a conventional plug-flow microreactor and a TAP reactor, we have found evidence that chrome oxides, in the presence of CHF_2Cl, undergo at least two separate surface transformations before becoming catalytically active toward disproportionation. The first transformation involves a reductive deoxygenation of high-valent surface-Cr species resulting in the formation of CO_2 and other oxidized products. This reduced surface then reacts with CHF_2Cl to form CO and a halogenated, catalytically active surface. It is proposed that catalysis occurs on coordinatively unsaturated halogenated Cr^{3+} active sites. An increase in Lewis acidity of the catalyst surface was shown to accompany each transformation step. A brief kinetic study of the disproportionation gave evidence that the reaction does not proceed by a Rideal–Eley mechanism. Examination of initial product distributions, arising from a CHF_3-activated catalyst, gave evidence that is consistent with a monomolecular halogen-exchange mechanism. © 1993 Academic Press, Inc.

INTRODUCTION

The disproportionations of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) have been reported to be catalyzed by a variety of metal oxides and halides (*1–10*):

$$2\ RR'CFCl \rightarrow RR'CF_2 + RR'CCl_2, \quad (1)$$

where R, R′ = alkyl, H or halogen. However, the mechanisms of these disproportionations have been ill-defined. Proposed mechanisms may be grouped into three classes. Included are those mechanisms whose principal bond making/breaking processes comprise (a) concerted, bimolecular halogen-exchange reactions between adsorbed organic species (*1–3*); (b) concerted halogen-exchange reactions between a free organic species and a polarized, complexed species (Rideal–Eley mechanism) (*4–6*); and (c) concerted, monomolecular exchanges of organic halogen with a metal halide surface (*7–10*). Class (c) mechanisms may be distinguished from the others by the fact that only these mechanisms involve the making and breaking of metal–halide bonds. Proponents of classes (a) and (b) mechanisms have suggested that the active sites of the catalysts are Lewis acid centers capable of strongly polarizing the adsorbed CFC or HCFC prior to reaction. This feature could also be included in class (c) mechanisms, however, Kemnitz *et al.* (*9, 10*) have suggested that Lewis acid sites are not required by these mechanisms and are unlikely to be necessary. They support this suggestion by their finding that CFCs are only weakly adsorbed on the surfaces of certain metal halides and oxides known to catalyze these reactions.

The empirical finding (*11*) that catalysts for the disproportionation of the CFCs and HCFCs are usually the same ones found active in isomerizations and halogenations of these compounds suggests that the active sites for *all* of these processes are the same or very similar. To the extent that these

0021-9517/93 $5.00

mechanisms are related, studies of the mechanisms of these other processes could yield information quite relevant to disproportionation mechanisms. The elegant work being carried out by Webb, Winfield, and their co-workers (*12–15*) on the fluorination of CFCs catalyzed by chromia is a case in point. Using isotopic-labeling techniques, these workers have been examining the halogenation reactions of chlorofluoroethanes catalyzed by chromia. By using ^{18}F- and ^{36}Cl-labelled hydrogen halides and CFCs, they have shown that halogenation of chlorofluorocarbons occurs at the catalyst surface through a halogen-exchange reaction. Reaction of a chlorofluorocarbon with catalytically active fluorination sites was shown to result in the formation of chlorination sites on the catalyst surface. It was also shown that chromia catalysts contain at least two types of halogenated sites: (1) sites inactive in halogenation of CFCs (suggested to be Cr(III)X_n, where X = F or Cl) and (2) sites active towards halogen-exchange with a CFC molecule (suggested to be Cr(IV)X_n or Cr(VI)X_n where X = F or Cl). Other workers have made similar, though less defined, proposals for CFC fluorination mechanisms. For example, Kolditz *et al.* (*5*) have offered ESR evidence for the possibility of a redox mechanism involving Cr^{3+}, Cr^{4+} and Cr^{6+} in CFC fluorinations. Finally, as with disproportionations, it has been proposed (*1*) that fluorination catalysts must possess Lewis acidity to account for their activity.

There have been few kinetic studies of CFC or HCFC disproportionations. In an early paper Gambaretto (*16*) reported that the disproportionation of CHF_2Cl over AlF_3 is first order in reactant. However, no mechanism was proposed to account for this finding. Cavaterra *et al.* (*8*) reported that the disproportionation of $CHFCl_2$ over AlF_3 followed kinetics consistent with successive reactions of $CHFCl_2$ and CHF_2Cl with Al–F and Al–Cl sites on the catalyst. Adsorption/desorption phenomena were not considered in their model. Kemnitz and Hess (*3*) studied the kinetics of disproportionation of CHF_2Cl over activated γ-Al_2O_3 and found the reaction orders to be greater than unity in the organic reactant. This finding was offered as support for a class (a) mechanism. Finally, Okazaki (*6*) studied the disproportionation of $CFCl_3$ over $FeCl_3$ on charcoal and found the kinetics obeyed a Rideal-Eley mechanism where the rate-determining step involved the reaction of complexed $CFCl_3$ with free $CFCl_3$.

In view of the uncertainties surrounding the mechanisms of these disproportionations, we decided to examine a simple example of such a reaction with the hope of attaining a better understanding of their mechanisms. We chose to examine the disproportionation of CHF_2Cl catalyzed by chromia. Our reasons for choosing this system were threefold. First, this system offers a simple product distribution compared to those found for two-carbon systems. Secondly, this disproportionation was found to be readily achievable at temperatures far below those needed to properly activate the catalyst, thus allowing us to cleanly separate the disproportionation from catalyst-activation processes. Finally, we have felt that an understanding of the mode of behavior of chromia catalysts is of key importance. Since these catalysts have been ubiquitous throughout CFC and HCFC chemistry, we have felt that any understanding of their mode of action in one arena of this chemistry would likely favorably impact the understanding of the others.

EXPERIMENTAL

Catalyst Preparation and Characterization

Two chromia-based catalysts were used in this study. One, designated here simply as Cr_2O_3, is a form of α-Cr_2O_3 prepared by the pyrolysis of ammonium dichromate. A sample of this pyrolyzate was pulverized, using a ball mill, to an average particle size of 50 to 75 μm. This material was then washed with warm water and filtered. The resulting solid was dried at 423 K, pressed (at 20,000 psi) into wafers, crushed and sieved into particles of average size of 250 to 425 μm. The BET surface area of this material, using N_2, was found to be 41.4 m^2/g. A pore volume, based on nitrogen adsorption, of 0.23 ml/g was found. X-ray diffraction (XRD) powder diffractograms showed that the material contained only α-Cr_2O_3. No other crystalline phases could be detected, however, the relatively high surface area suggests the presence of amorphous phases. Transmission electron microscopy revealed a solid consisting of aggregates of platelets consistent with the expected presence of microcrystalline α-Cr_2O_3 (*17*). X-ray photoelectron spectroscopy (XPS), using a VG Scientific spectrometer and Mg $K\alpha$ radiation, showed the surface of this material to consist of essentially pure Cr_2O_3 (*18*) containing *ca.* 3 to 4% surface carbon. Analysis for trace metals, using an atomic emission spectroscopic technique, revealed the presence of Ca (275 ppm) and Fe (66 ppm), in addition to Cr. No other metals were found (limits of detection: <0.5 ppm).

The other catalyst, designated here as Cr_2O_3(C) and possessing commercial utility (*19*), was also prepared from ammonium dichromate pyrolyzate, following the same water wash and drying operations applied to Cr_2O_3. The resulting solid was then compounded with 5.9 wt% of chromium hydroxyacetate $[Cr_3(OH)_2(OAc)_7]$, water and 2 wt% graphite to produce a final catalyst that was pelletized, following a drying step at *ca.* 423 K. This material was then crushed and sieved into particles possessing average sizes of 250 to 425 μm. This final catalyst possessed a surface area of 43.1 m^2/g by the BET method, using N_2. The nitrogen adsorption-based pore volume was found to be 0.20 ml/g. XRD showed this material to be indistinguishable from α-Cr_2O_3. XPS yielded spectra consistent with Cr_2O_3 containing *ca.* 7% surface carbon.

A titration technique was used for measuring the presence of high-valent ($>3^+$) chromium on the surfaces of the chrome catalysts being studied. This technique, based on a literature technique (*20*), consists of titrating (with aqueous $Na_2S_2O_3$) the iodine formed by the reaction of oxidizing surface species with aqueous I^-. We improved the convenience of the technique by adding the required amount of HCl near the end of the period that the sample had stood in aqueous KI rather than at its beginning. This modification minimized the need to exclude oxygen from the system. Since the valencies of the high-valent chrome species studied were unknown, the oxidizing capacity of each sample is expressed as Faradays transferred (or equivalently, of μmoles of I^- oxidized) per gram of catalyst.

Reactors and Instrumental Analysis Techniques

Reactions at atmospheric pressures were studied using a 6″ × ¼″ stainless-steel microreactor heated by an air-stirred silicon carbide bath. Gases were fed to the reactor using calibrated Tylan mass flow controllers. All flows are referenced to standard temperature and pressure conditions of 273 K and 101.3 kPa. Analysis of the reaction products was accomplished using a Hewlett Packard Gas Chromatograph Model 5708A equipped with a 5% Krytox on 60/80 Carbopak BHT 20′ × ⅛″ column. Catalyst samples (0.5 to 1.0 g) mixed with 600–700 μm silicon carbide (3.5 to 4.0 g), acting as an inert diluent, were used in the reactor. Catalyst activation was carried out by passing a given gas, diluted with N_2, over the catalyst at elevated temperatures for a specified time period. Catalyst activities were measured by flowing a 13% mixture of CHF_2Cl in N_2 over the treated sample at 323 K with a contact time of 0.27 s. Kinetic measurements were carried out on a mixture of 1.0 g of Cr_2O_3(C) and 3.4 g SiC placed in the microreactor. The catalyst was activated by treatment with a stream of 13% CHF_2Cl in N_2 at 463 K for 16 h. All kinetic measurements were carried out at 296 K in the differential mode with all reactant conversions kept below 9%. The feed flowrates were held constant at 20 cc/min. These conditions were chosen to minimize the contribution of an apparent catalyst poisoning reaction that was significant at higher temperatures. In spite of these precautions, slow catalyst deactivation was still noted and the data was corrected to reflect this using periodic catalyst activity measurements.

Many of our experiments were performed using a TAP (temporal analysis of products) reactor. Since a detailed description of this system is available elsewhere (*21*), only key features pertinent to this study are given here. The reactor system basically consists of (a) a gas supply system as provided by two high-speed pulse valves and one continuous flow valve, (b) a 1.25″ × 0.25″ reactor containing a packed catalyst bed, and (c) a product gas analysis system as provided by a quadrupole mass spectrometer (UTI 100C). Experimental setup, data acquisition and signal processing were performed on an HP-320 micro computer. The catalyst loadings in this study were generally 0.07 to 0.10 g and were placed in the reactor between two charges of *ca.* 0.20 to 0.30 g each of glass beads of the same particle size. In this study, the quantities of gas passed through the pulse valves were *ca.* 1 to 10 nmol/pulse.

The TAP reactor system offers several advantages over conventional pulsed-reactor systems. Because gases may be pulsed into the reactor at pressures as low as *ca.* 10^{-7} Torr (1 Torr = 133.32 Pa), the contact times of the gases are quite small—of the order of milliseconds. Also, at the low pressures used, gas–gas collisions are considerably reduced. Both of these features offer the possibility of identifying metastable or unstable intermediates not usually observed in a conventional reactor. Another advantage follows from the amount of gas contained in a typical pulse. The pulse valves permit a range of quantities of gas of *ca.* 0.10 to 100 nmol/pulse. This corresponds to the equivalent of *ca.* 10^{-6} to 10^{-3} of monolayer surface coverage of a typical 0.1g catalyst loading possessing a surface area of 50 m^2/g. Thus, under these conditions, the catalyst may be treated either as a constant or slowly diminishing reactant, depending upon the quantities of gas being fed. In either case, the small quantities of reactants fed permits the surface chemistry of the catalyst to be studied independent of the catalysis. Finally, the low gas pressures and small surface coverages lead to little, if any, surface inhibitions of reactions by most adsorbed gases. This often leads to simplifications in the kinetic expressions used to describe the reactions taking place.

Since the compositions of gases exiting a TAP reactor are analyzed using a mass spectrometer, complications in this analysis often arise due to the overlapping of certain fragmentation patterns from different compounds. Because of this we had to use a matrix algebraic technique employing the relative intensities of several representative m/e-values (in this work, *m/e* = 40, 51, 67, 69, and 83) to define the composition of a mixture of CHF_2Cl and its disproportionation products. Argon (*m/e* = 40) was used as an internal standard (20 mol%). Figure 1 shows typical pulse profiles measured at m/e values corresponding to CHF_2Cl and disproportionation products obtained from pulsing CHF_2Cl over activated Cr_2O_3 at 473 K. The principal contributors to each m/e value are indicated in parentheses.

The TAP reactor was also used to carry out temperature-programmed reaction and desorption studies. In the temperature-programmed reaction mode of operation, a gas was pulsed over a catalyst while the temperature was increased at a constant rate while monitoring a given m/e value. For temperature-programmed desorption, we monitored the rate of desorption of gas from a previously-saturated surface as a function of temperature by monitoring a particular *m/e* value characteristic of an adsorbed gas.

Analyses of the reactions of CHF_2Cl with Cr_2O_3(C) were also performed on a DuPont 950 Thermal Analyzer. The product gases were analyzed by mass spectroscopy. The sample was first heated in a helium flow (2.0 ml per minute) to 973 K and cooled to room temperature. The TGA-MS experiment was started while flowing 1.5 ml CHF_2Cl/min

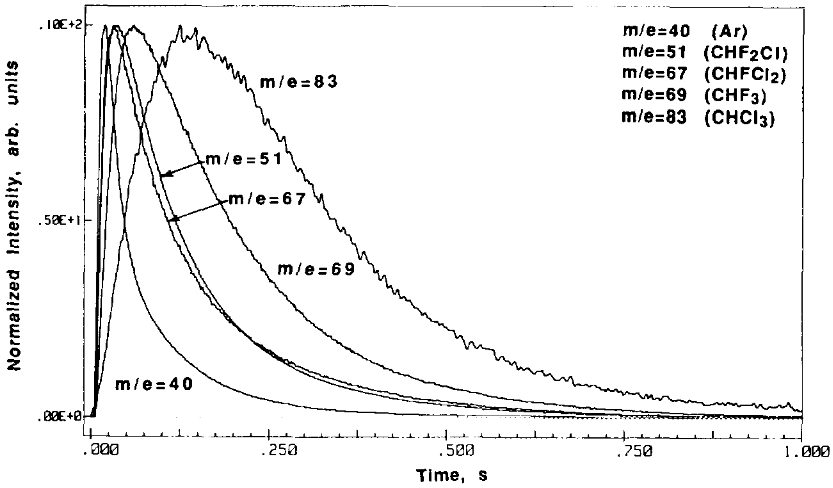

FIG. 1. Pulse profiles of CHF_2Cl and its disproportionation products over Cr_2O_3 at 473 K.

and 0.5 ml He/min through the sample region. The temperature of the sample was increased linearly at a rate of 10 K/min. Mass spectra were taken every minute giving a temperature resolution of the product gas analysis of one spectrum per 10 K.

Reagents

All reactant gases were obtained from commercial sources and were used as received without further treatment. The gases used were N_2, O_2, $^{18}O_2$ (97%), ^{13}CO (99.4%), H_2, HCl, HF, CF_3Cl, CF_4, CCl_4, CF_3CF_3, CHF_3, CHF_2Cl, $CHFCl_2$, $CHCl_3$, CH_3OCH_3, and Ar.

RESULTS

Activity Studies

The disproportionation of CHF_2Cl over the chromia catalysts was always accompanied by a further disproportionation of one of the co-products, $CHFCl_2$ (*3*, *22*):

$$2\ CHF_2Cl \rightarrow CHF_3 + CHFCl_2 \quad (2)$$

$$2\ CHFCl_2 \rightarrow CHF_2Cl + CHCl_3. \quad (3)$$

These reactions were usually found to proceed cleanly in the presence of the chromia catalysts. At elevated temperatures, equilibrium (at conversions of *ca.* 90 to 95%) could be approached with less than 1% of byproduct formation. However, the reactions were generally studied at extents of reaction well removed from equilibrium. Both of the Cr_2O_3 and Cr_2O_3(C) catalysts displayed similar overall activities suggesting that the same or similar active sites were operating in both catalysts.

Early in our studies it was noted, as others have found (*1*, *23*) for related systems, that the chrome catalysts used here required an activation procedure to realize their catalytic activity. Usually, heating the catalysts to temperatures above *ca.* 448 K for extended periods of time in the presence of CHF_2Cl itself was sufficient to create an active catalyst. However, it was soon found that many other substances served to activate these catalysts. Tables 1 and 2 describe the relative effectiveness of several substances as activators of the Cr_2O_3 and Cr_2O_3(C) catalysts toward disproportionation. In these and later tables the activities of the catalysts are measured by their effectiveness in converting CHF_2Cl to CHF_3. While, strictly speaking, catalyst activity is directly proportional to percent conversion of CHF_2Cl to CHF_3 only at the limit of zero percent conversions, we have felt that this

TABLE 1

Disproportionation Activities of Cr_2O_3(C) Following Treatment[a] with Various Substances

Treatment gas	% Conv. to CHF_3
N_2	<0.01
CHF_2Cl	39.1
CHF_3	53.2
$CHCl_3$	1.1
CCl_4	1.7
CF_3CF_3	29.2
HCl	0.1
HF	0.04

[a] Cr_2O_3(C) (3.7 g) treated with 20% treatment gas in N_2/698 K/1 h.

measure of catalyst activity is an adequate measure for ranking the effects studied here.

Tables 1 and 2 show that all of the effective activators, except for HF and CF_3Cl, may also be expected to be the most effective reducing agents. Also, flushing with N_2 after some treatments was necessary to expose the catalysts activity, presumably due to strong adsorption of activation products. The effectiveness of HF as an activator might be linked to the fact that HF, as usually supplied, contains small amounts of H_2, a demonstrated catalyst activator. We attempted to demonstrate this by flushing the hydrogen out of our HF source. However, we were apparently unsuccessful since, even after an overnight purge of our HF cylinder, catalytic activity remained significant after treatment with this source of HF, albeit with a significant induction period. The reason for the effectiveness of CF_3Cl was not apparent from this test and shall be discussed further under the TAP reactor section. Of particular interest was the finding that a non-halogen-containing compound (CO or H_2) could be an effective catalyst activator.

TABLE 2

Disproportionation Activities of Cr_2O_3 Following Treatment[a] with Various Substances

Treatment gas	% Conv. to CHF_3
N_2	<0.01
CHF_3[b]	63.1
$CHCl_3$[c]	23.6
CF_3Cl	47.6
CF_4	0.5
CCl_4[e]	2.2
HF[c,d]	23.7
CO	46.5
H_2	23.5

[a] Cr_2O_3 (0.5 g) treated with 20% treatment gas in N_2/698 K/1 h.

[b] Catalyst wt = 1.0 g.

[c] Catalyst flushed with N_2 for 1 h at 698 K following treatment.

[d] Induction period (*ca.* 1 h) observed.

[e] Activation temperature = 523 K.

The observation that chromium oxide could be activated using a reducing agent such as CO, led us to perform experiments determining the effects of a series of treatments on a single catalyst sample. These treatments consisted of flowing certain gases over a sample of Cr_2O_3 for 1 h at a specified temperature. Disproportionation activity was then tested at 323 K following each treatment. Of particular interest was learning whether or not an activated sample could have its catalytic activity quenched and then reactivated. Table 3 summarizes our findings.

The results of Table 3 are strong evidence

TABLE 3

Successive Disproportionation Activities Following Various Treatments of Cr_2O_3[a]

Treatment step	Catalyst treatment	% Conv. to CHF_3
1	N_2/698 K	0
2	20% CO in N_2/698 K	9.8
3	22% O_2 in CHF_2Cl/N_2/323 K	8.8
4	20% O_2 in N_2/698 K	0
5	20% CO in N_2/698 K	34.1

[a] Cr_2O_3 (0.5 g) was treated with each gas at 0.27 s contact time for 1 h.

that an oxidation/reduction cycle is involved in the destruction and creation of active sites for this catalysis. Apparently, the active sites on a chromium oxide catalyst can be created by reduction of surface sites by CO and destroyed by oxidation of these sites with O_2. However, at 323 K, O_2 does not apparently affect the catalysis significantly. Finally, the catalytic activity could be restored, and even enhanced, by treatment with CO at elevated temperatures following treatment with O_2 at 698 K.

The effect of water on CO-reduced Cr_2O_3 was examined separately. In this case, a sample of CO-reduced Cr_2O_3 was treated with a stream of 3% H_2O in N_2 for $\frac{1}{2}$ h at 698 K. Following this treatment the system was flushed with dry N_2 for an additional 1 h at 698 K in an attempt to drive off any absorbed water. A test of catalytic activity at 323 K showed a 47% reduction in activity, compared to a control sample.

The effects of added gases on the disproportionation of CHF_2Cl were also of interest in helping to describe the nature of the active sites for this reaction. In a brief study of these effects it was found that when the disproportionation of CHF_2Cl over $Cr_2O_3(C)$ was carried out in the presence of *ca.* 10% dimethyl ether, a Lewis base, the reaction was completely inhibited. When the dimethyl ether was removed from the feed, the catalyst remained inactive. This suggests that the active sites for the disproportionation are Lewis acid sites. A weaker effect was noted with both CO and CO_2. A mixture of 13% of either CO or CO_2 and 13% CHF_2Cl in N_2 when passed over an active catalyst at 323 K showed *ca.* 67% or 40%, respectively, of the activity shown in the absence of the added gas. The original catalyst activity was completely restored on replacing the CO by N_2, however, only *ca.* 70% of the original activity returned on replacement of the CO_2 by N_2. Finally, HCl, when added to the feed at concentrations of *ca.* 10% at 323 K, completely quenched the catalysis.

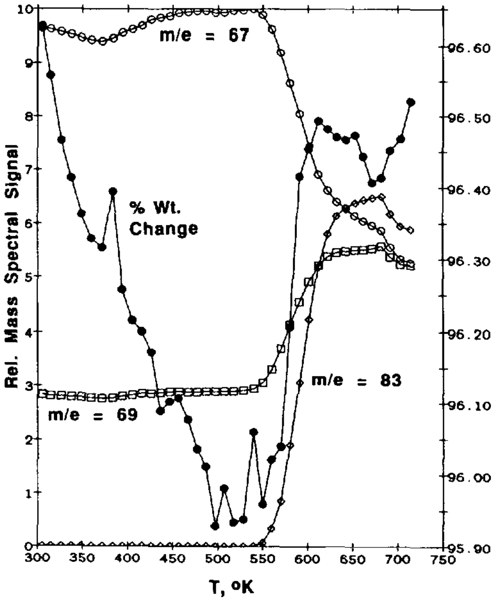

FIG. 2. TGA-MS spectra of products arising from reaction of CHF_2Cl with $Cr_2O_3(C)$.

Thermogravimetric Analysis-Mass Spectroscopy (TGA-MS)

In an effort to learn more about the transformations accompanying catalyst activation, the activation of $Cr_2O_3(C)$ was followed by TGA-MS, monitoring the weight of the sample as a function of temperature. In addition, the evolution of the gas composition, as a function of temperature while flowing CHF_2Cl gas, was followed. In Fig. 2 a typical TGA-MS spectrum is shown. Three m/e values, each characteristic of each of two of the products and CHF_2Cl, and the relative change in sample weight are shown as a function of temperature. A sudden increase in weight of the sample at approximately 573 K was observed, which can be ascribed to the uptake of halogen by the chromium oxide. The observed decrease in weight when raising the temperature from 313 K to 573 K is due largely to a baseline drift of the instrument. Accompanying the sample weight increase at *ca.* 573 K, conversion of CHF_2Cl to the disproportionation products CHF_3 (*m*/*e* = 69) and $CHCl_3$ (*m*/

TABLE 4

XPS Binding Energies (eV) and Atomic% Composition of Treated Samples of Cr_2O_3[a]

Treatment gas	C 1*s*	F 1*s*	O 1*s*	Cr $2p_{3/2}$
N_2	284.6 (3.9)	— (<0.6)	529.8 (58.6)	576.3 (36.0)
HF	284.6 (3.5)	684.2 (10.7)	529.9 (50.6)	576.4 (35.2)
CHF_3	284.6 (3.4)	684.3 (8.0)	530.2 (52.4)	576.7 (36.3)

[a] Samples were exposed to a flow of 13% treatment gas in N_2/1 h/698 K. Numbers in parentheses represent atomic % composition. Binding energies are based on C 1*s* binding energy of 284.6 eV.

e = 83) was observed, suggesting that an uptake of halogen by the catalyst coincides with the onset of catalytic activity. The decrease in intensity of the *m/e* = 67 peak can be mainly attributed to the loss of CHF_2Cl.

Surface Analysis

In an effort to understand the effects of the treatment gases on the surface of Cr_2O_3, an XPS analysis was carried out on samples which had separately been treated at 698 K with N_2, CHF_3 and HF. The samples were never exposed to air throughout the procedure. The bonding energies found for Cr and O were consistent with those reported for α-Cr_2O_3 (*18*). No evidence for valence states of Cr other than 3^+ could be found in any of the samples. The binding energies found for fluorine were consistent with those previously found for surface chromium fluorides (*2*). The O : Cr ratio decreased as the extent of surface fluorination increased. Thus, the surfaces of both the CHF_3- and HF-treated Cr_2O_3 samples apparently contained significant amounts of chromium fluorides. Table 4 summarizes our findings.

Similar results were obtained from Cr_2O_3(C). Surface area measurements carried out on the treated samples of Cr_2O_3(C) showed the surface areas of the HF- and CHF_3-treated samples to have changed by less than 10% from that measured (43.1 m^2/g) for the N_2-treated sample.

Microreactor Kinetics

The kinetic behavior of the disproportionation was briefly investigated using Cr_2O_3(C) in an effort to distinguish between various possible mechanisms. Table 5 summarizes our findings.

We examined the fit of only one kinetic model derived from a class (b) mechanism, described in the introduction. In this model, the rate-determining step was defined as the reaction of free CHF_2Cl with surface-bound CHF_2Cl. This model did not give a satisfactory fit to the data. Class (a) mechanisms were not examined since the independent information, *vide infra*, indicated that these mechanisms were not operative. Kinetic models corresponding to a class (c) mechanism, where the rate-determining steps involved either carbon–halogen bond breaking/making or product desorption, were constructed but not tested. These models involved reaction, adsorption and desorption processes of each of the four HCFCs with two postulated halogenated metal sites. These sites were distinguished by the nature of the exchangeable halogen bonded to each site. The resulting models consisted of 14 separate processes. A portion of one of the models, involving the processes associated with CHF_2Cl is shown in Scheme 1.

(1) $CHF_2Cl + S\text{-}F = CHF_2Cl{*}S\text{-}F$
(2) $CHF_2Cl{*}S\text{-}F = CHF_3{*}S\text{-}Cl$
(3) $CHF_3{*}S\text{-}Cl = CHF_3 + S\text{-}Cl$
(4) $CHF_2Cl + S\text{-}Cl = CHF_2Cl{*}S\text{-}Cl$
(5) $CHF_2Cl{*}S\text{-}Cl = CHFCl_2{*}S\text{-}F$
(6) $CHFCl_2{*}S\text{-}F = CHFCl_2 + S\text{-}F$

S–Cl and S–F represent halogenated catalyst sites

SCHEME 1. Halogenated-Site Mechanism

TABLE 5

Product Partial Pressures from Disproportionation of CHF_2Cl

CHF_2Cl[b]	CHF_3[a]	$CHFCl_2$[a]	$CHCl_3$[a]
0.716	0.480	0.034	0.237
0.717	0.516	0.045	0.258
1.83	0.840	0.092	0.388
1.90	0.796	0.073	0.365
3.30	1.04	0.109	0.460
3.40	1.04	0.134	0.463
6.64	1.31	0.180	0.637
6.67	1.53	0.234	0.666
9.85	1.70	0.243	0.751
10.0	1.62	0.275	0.700
10.1	1.60	0.244	0.760
10.2	1.65	0.316	0.766
20.2	2.01	0.374	1.03
20.6	2.42	0.434	0.912
44.3	3.07	0.589	1.12

[a] Partial pressures = atm × 10^3 (1 atm = 101.3 kPa).
[b] Partial pressures = atm × 10^2.

This model yielded an expression for the rate of formation of CHF_3 that contained fourteen adjustable parameters. After combining certain parameters, while still retaining the sense of the model, and requiring that the net halogen content of the catalyst remain constant, an expression with nine parameters was finally obtained. With such a large number of adjustable parameters remaining, any attempt to fit this model to the limited data available was considered imprudent. As a result, it was possible to eliminate only the Rideal–Eley mechanism (class (b) mechanism) described in the introduction.

Attempts to measure activation energies of the disproportionation failed, presumably due to the formation of an unknown substances (HCl?) which slowly poisoned the catalysis at elevated temperatures. However, at temperatures above *ca.* 448–473 K the reaction rates sharply accelerated, possibly due to the desorption of this poison from the catalyst surface.

TAP Reactor Studies

(*a*) *Catalyst activation.* The reactions of CHF_3 and CHF_2Cl with Cr_2O_3 were first examined in an attempt to identify the gaseous products formed during the catalyst activation process noted earlier. Pulsing either of these gases over Cr_2O_3 at temperatures between 523 and 798 K resulted in significant reaction. For example, pulsing CHF_3 over Cr_2O_3 at temperatures between 698 and 798 K yielded increased pulse intensities for certain *m/e* values indicating the formation of H_2O, HF and CO_2. CO was also observed, however, this could not be distinguishable from a signal resulting from backscattering processes occurring at the ion-pump. The formation of COF_2 could not be ruled out since COF_2 possesses *m/e* values coinciding with CHF_3. However, only very small amounts of COF_2 could have been present since the pulse shapes at the relevant *m/e* values were essentially identical to those previously measured for CHF_3. The formation of oxygenated products implies the concurrent formation of surface metal fluorides, as was confirmed previously by our XPS studies. Similar results were obtained with the more reactive CHF_2Cl indicating surface halogenation and formation of oxygenated gaseous species occurred here as well.

The formation of CO_2 upon pulsing CHF_3 over Cr_2O_3 suggested that our Cr_2O_3 sample contained oxidizing sites (Cr^{4+} or Cr^{6+} ?) that were reduced by the CHF_3. To test this we pulsed CO over Cr_2O_3 at elevated temperatures and found that indeed CO_2 was readily formed, indicating the reduction of surface sites. Figure 3 shows a comparison between the CO_2 formed (based on *m/e* = 44) from CHF_3 pulsing and from CO pulsing at 798 K. The amount of CO_2 formed from CO treatment (15.1 μmoles/g) was approximately three times that formed from CHF_3 (4.6 μmoles/g). This may have occurred, in part, because of differences in the thermal stabilities of the samples (*24*). Support for this possibility came when we observed *more* CO_2 formed from CHF_3 at 698 K (12.1 μmoles/g) than at 798 K (4.6 μmoles/g), suggesting that thermal depletion of the oxidation potential was less significant at lower temperatures.

Chromium oxides, prepared by the pyrol-

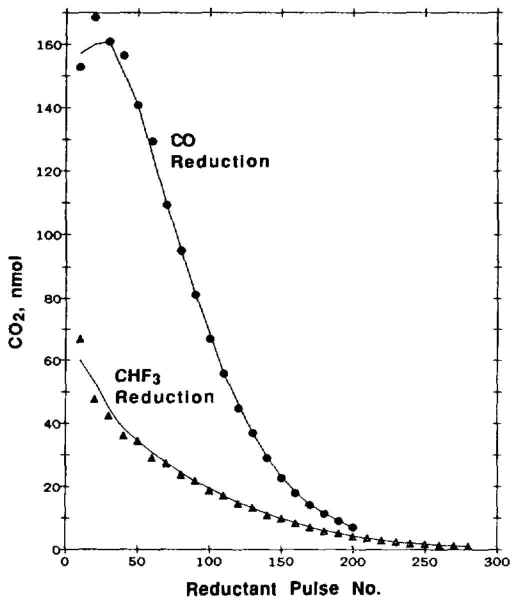

FIG. 3. Carbon dioxide formation from reductions of Cr_2O_3 by CHF_3 and CO at 798 K.

ysis of ammonium dichromate, are well known to contain significant amounts of high-valent surface Cr species (*20, 25*). Most of these species consist of water-soluble Cr^{6+} compounds, extractable by simple water washing. Since our catalysts had been thoroughly washed during their preparation, any high-valent chrome species remaining were not water soluble. This suggested that the high-valent chrome species remaining on Cr_2O_3 were not separate Cr^{6+} oxide phases but may have consisted of mixed Cr^{m+}/Cr^{n+} ($n, m = 3, 4, 5,$ or 6) or pure Cr^{4+} or Cr^{5+} oxide phases which are less likely to be water soluble. As a further test for the presence of high-valent Cr species on Cr_2O_3 we found, on applying the iodometric titration test, that a sample of Cr_2O_3 yielded an oxidation capacity of 6.2×10^{-5} Faradays/g. This compares to a value of 3.0×10^{-5} Faradays/g obtained from the CO-oxidation technique. The lower value obtained using the CO-reduction technique may have been due to a loss of oxidation capacity resulting from the thermal treatment of the sample (*24*). This was checked by measuring the oxidation capacity of a sample that had been exposed to N_2 for 1 h at 698 K and found to give an oxidation capacity, using the iodometric technique, that was 15% of an unheated sample. Based on these values and the reported surface area ascribed to a monolayer of 1 g of Cr_2O_3 (*26*), we estimate that the percentage of surface Cr atoms that are in valence states greater than 3^+ ranges from 1.4 to 8.4%, depending upon the analysis technique used and the valence states of the Cr. Finally, testing of the aqueous phase of a water-washed sample of Cr_2O_3 by the iodometric test showed the absence of any high-valent Cr, verifying the absence of water-extractable chromates for this material. As expected, testing of this water-washed Cr_2O_3 as a disproportionation catalyst showed no decline in activity compared to an unwashed sample.

As noted above, our microreactor studies showed that the catalysis could be quenched by treatment with oxygen at 698 K. In order to study the reaction of oxygen with the catalyst in more detail, we investigated the oxidation of active catalysts with O_2 in the TAP reactor. A sample of Cr_2O_3, previously reduced with CO at 698 K, was pulsed with O_2 and an uptake of O_2 was observed. The oxidized catalyst was again reduced with CO and, finally, again oxidized with O_2. The progress of these redox reactions was followed by measuring the maximum signal intensity of each pulse of gas (at $m/e = 44$ and 32) as a function of pulse number. Figure 4 shows the results of this experiment. The reproducibility of the cycle shows the complete reversibility of both the reduction and oxidation processes at 698 K. The relative stability of the system was also demonstrated by the observation that the extent of CO uptake by the Cr_2O_3 was unchanged after standing for 10 min at 698 K. In a similar study, involving the oxidation of CO-reduced Cr_2O_3 with $^{18}O_2$, it was noted that when the catalyst was allowed to stand for eight minutes at 798 K, a sharp increase in oxygen uptake occurred. This phenomenon

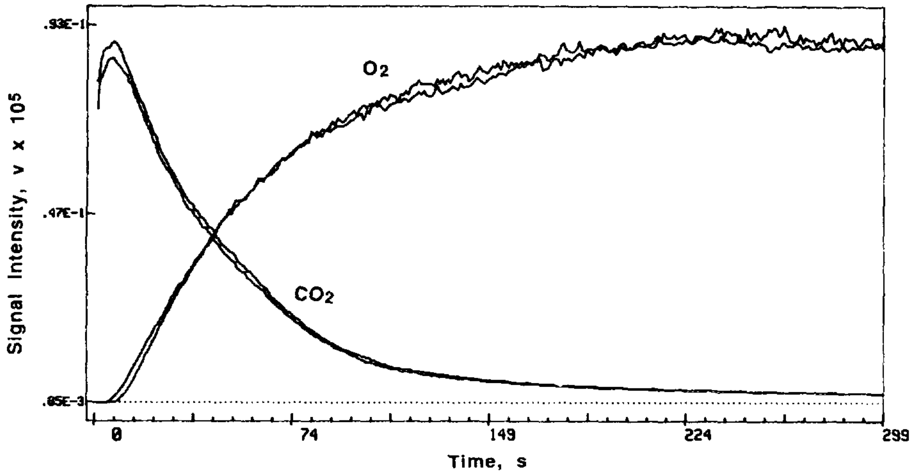

FIG. 4. Redox reactions of Cr_2O_3 as function of pulse number at 698 K.

suggests that the surface oxygen atoms, at this higher temperature, are either highly mobile and diffuse away from the active sites leaving vacancies behind or that they desorb relatively easily.

As noted earlier in our microreactor studies, treatment of Cr_2O_3 with CF_3Cl at 698 K/1 h was sufficient activation for F-22 disproportionation to occur. This result was unexpected since it was hard to see how CF_3Cl could reduce Cr_2O_3, as hypothesized for our activation process. In an attempt to shed more light on this particular activation process we examined the reaction of CF_3Cl with Cr_2O_3 in the TAP reactor. Upon pulsing CF_3Cl over a sample of Cr_2O_3 that had been heated to 698 K we observed the formation of large amounts of CHF_3, identified by its characteristic mass spectra, and smaller amounts of CO_2 and H_2O. Since we already knew that CHF_3 was an effective activator of Cr_2O_3, this finding was sufficient to explain the formation of an activated catalyst following this treatment. However, the source of hydrogen has remained unknown. Possibly, hydrogen from surface hydroxyl groups reacted with CF_3Cl with an accompanying oxidation of an associated Cr site. The newly-formed CHF_3 could then reduce already-existing high-valent Cr centers to form the active catalyst sites. To test this we next treated a sample of Cr_2O_3 with a flow of oxygen at 698 K in an attempt to oxidatively remove any such surface hydroxyl groups and any other surface reducing agents. Following this, we pulsed CF_3Cl over the freshly-treated Cr_2O_3 and found no evidence of gaseous reaction products. Separately, a parallel experiment was carried out in our microreactor whereby a sample of Cr_2O_3 was treated with 20% O_2 in N_2 at 698 K/1 h prior to treatment with 20% CF_3Cl in N_2 at 698 K/1 h. Testing of the resulting catalyst under our standard test conditions at 323 K revealed an activity that was only 6% of the activity obtained previously from a CF_3Cl-activated catalyst obtained *without* pretreatment with O_2. From these results we conclude that CF_3Cl alone does not appear to reduce Cr_2O_3 under these conditions but requires the presence of unknown surface reducing agents, such as hydroxyl groups.

In microreactor studies both Cr_2O_3 and $Cr_2O_3(C)$, following activation by CO at 698 K, proved to be active catalysts for disproportionation of CHF_2Cl at temperatures as low as 296 K (see Table 5). Under such mild conditions the formation of metal halide surface sites might be questioned. To explore

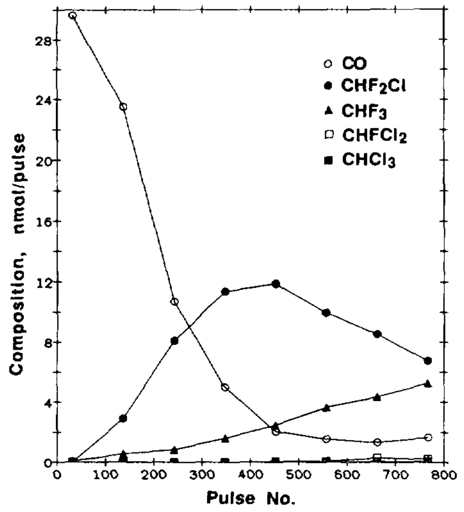

FIG. 5. Reaction of CHF$_2$Cl with CO-reduced Cr$_2$O$_3$ as a function of pulse number.

this question we examined the reaction of CHF$_2$Cl with CO-reduced Cr$_2$O$_3$ in the TAP reactor. We found that CHF$_2$Cl, when pulsed over CO-reduced Cr$_2$O$_3$ at temperatures as low as 348 K, reacted to form CO. When CHF$_2$Cl was pulsed over CO-reduced Cr$_2$O$_3$ at 523 K, CO (m/e = 28) was the *only* product observed, initially. On further pulsing new unidentified products began to appear. These compounds yielded m/e values of 69, 51, and 47 and were tentatively identified as the fragments CF$_2$OH, CF$_2$H, and COF. In order to verify that the CO was coming from CHF$_2$Cl and not from CO that had remained on the surface following the reduction step, we separately reduced Cr$_2$O$_3$ with ^{13}CO and showed that, upon pulsing CHF$_2$Cl over the reduced material, no evidence of enrichment of the natural abundance of the ^{13}C in CO was found. After additional pulsing of these systems, disproportionation products began to appear while the formation of CO declined. Mass spectral analysis of the products arising from a sample of CO-reduced CR$_2$O$_3$, following every 100 pulses, yielded the product composition evolution given in Fig. 5.

As seen from Fig. 5, the decline in the formation of CO appears to be matched by a corresponding rise in disproportionation activity as evidenced by the rising formation of disproportionation products and a decline in the CHF$_2$Cl reactant, following an initial rise in CHF$_2$Cl due to its decreasing reaction with the surface. This is direct evidence that the active sites of the catalyst are created by the reaction of CHF$_2$Cl with the reduced chromium oxide surface. Measurements of the carbon balance associated with the reaction showed that approximately half of the carbon fed to the catalyst remained bound to the surface following a pulse. This probably occurred because the disproportionation products were strongly absorbed on the surface. This explanation was supported when the individual products, upon pulsing over unactivated Cr$_2$O$_3$, yielded increasing pulse intensities as the temperature was raised above 523 K. Evidence that the chromium sites reacting were those that were previously reduced by CO, at a higher temperature, was found when it was noted that unreduced Cr$_2$O$_3$ did not significantly react with CHF$_2$Cl at 523 K to produce either CO or disproportionation products. Non-reduced Cr$_2$O$_3$ produced less than 4% of the CO produced by the reduced Cr$_2$O$_3$ at 523 K. Apparently, the CO that was produced by the nonreduced Cr$_2$O$_3$ at 523 K was coming from nascent reduced sites created by the reduction of Cr$_2$O$_3$ by CHF$_2$Cl, since low levels of CO$_2$ production were also observed at this temperature.

(*b*) *Catalytic activity.* In a search for a direct link between CO$_2$ formation and catalytic activity, we monitored the formation of CO$_2$, CHFCl$_2$, CHF$_3$, and CHCl$_3$ in the TAP reactor at 798 K during activation of Cr$_2$O$_3$ by CHFCl$_2$. The disproportionation of CHFCl$_2$ was examined since it was easier to follow the formation of these products by mass spectroscopy than those from CHF$_2$Cl disproportionation. Data were acquired by sequentially measuring the mass spectral intensity of each component formed following the pulsing of CHFCl$_2$ over the chrome oxide. Figure 6 presents the mass spectral

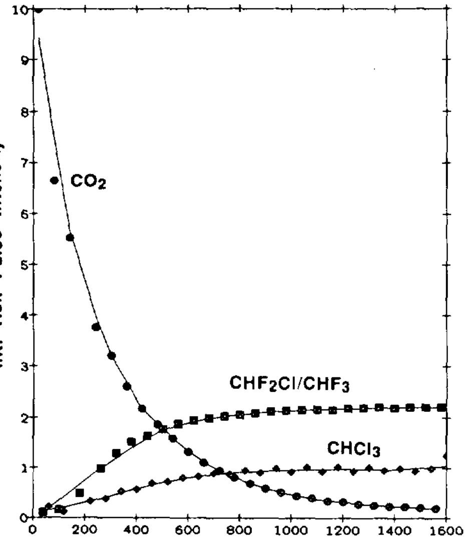

FIG. 6. Mass spectral areas *vs* pulse number for the reaction of $CHFCl_2$ with Cr_2O_3.

pulse areas for the three components: CO_2, $CHCl_3$, and CHF_2Cl/CHF_3. This figure clearly shows that as the formation of carbon dioxide decreases, the activity of the catalyst towards disproportionation increases. This experiment supports our presumption that the creation of active sites in disproportionation catalysis involves a reduction of high-valent chromium ions.

An experiment was carried out in which we sought to examine the disproportionation of CHF_2Cl at its earliest stages over a chrome oxide sample that had been activated by treatment with CHF_3. Catalyst activation was accomplished by treating 70 mg of Cr_2O_3(C) with a stream of 1 cc/min of CHF_3 at 682 K for 1 h. By this treatment, if surface metal halides were formed, only metal *fluorides* would have been possible. Pulsing CHF_2Cl (*ca.* 5.3 nmole/pulse) over this activated material at 561 K showed that initially mostly CHF_3 was formed. As the pulsing continued, increasing amounts of $CHFCl_2$ and $CHCl_3$ formed while the relative amounts of CHF_3 formed decreased. Figure 7 shows the pulse compositions as a function of number of pulses of CHF_2Cl introduced. While the F : Cl ratio was high (11.4) after 880 pulses, after 4000 pulses of CHF_2Cl the F : Cl ratio reached 2.30, close to the theoretical level of 2.0 required for the disproportionation. These results show that the disproportionation products can arise from independent reactions and are not formed in constant proportions as required by a bimolecular mechanism. We conclude that CHF_3-activated Cr_2O_3(C) initially contains sites capable only of fluorination of a reactive HCFC. One may assume that sites active towards chlorination are then gradually introduced as surface halogen exchange proceeds during the reaction with a HCFC.

(*c*) *Lewis acidity.* In our microreactor studies we showed that the disproportionation of CHF_2Cl was inhibited by dimethyl ether, presumably acting as a Lewis base blocking Lewis acid sites responsible for the catalysis. As a follow-up to this discovery, we compared the Lewis acidities of untreated Cr_2O_3 with those that had been reduced by CHF_3 or CO through a temperature-programmed desorption measurement of dimethyl ether carried out in the TAP

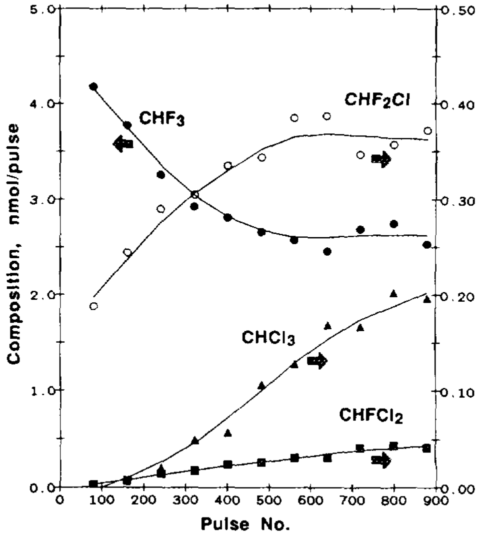

FIG. 7. Pulse composition as a function of number of CHF_2Cl pulses over CHF_3-treated Cr_2O_3(C).

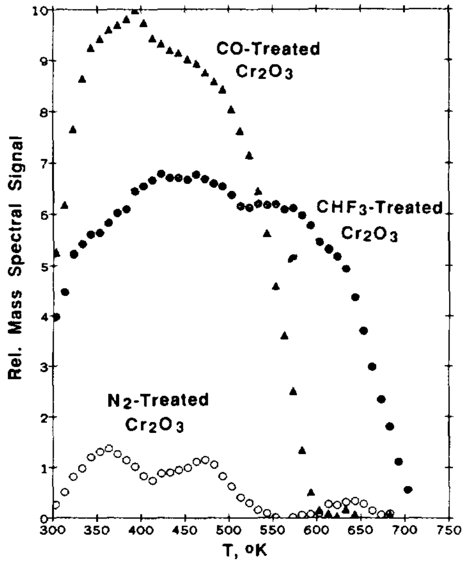

FIG. 8. Temperature-programmed desorptions of dimethyl ether from Cr_2O_3.

reactor. All of the samples were preheated to 798 K, treated with the appropriate treatment gas (none in the case of the untreated sample) and subsequently saturated with dimethyl ether at room temperature at 10^{-5} Torr. Following this, each sample was heated at 10°/min while monitoring the relative amounts of dimethyl ether desorbing by measuring $m/e = 46$ every second. Figure 8 shows the results obtained. As can be seen from this figure, treatment with either CO or CHF_3 greatly increases the population of Lewis acid sites. This is further support for the hypothesis that Lewis acid sites are necessary for catalysis to occur. Also, the extensive desorption at high temperatures shown by the CHF_3-treated sample suggests the presence of relatively strong Lewis acid sites, probably resulting from site fluorination.

Further support for the increase in Lewis acidity on reduction came from an examination of the peak shapes of CO_2 resulting from the reduction of Cr_2O_3 with CO. On pulsing untreated Cr_2O_3 with CO, very sharp CO_2-product pulses were detected initially that became broader as the extent of reduction (i.e., number of CO pulses injected) increased. The absolute width of the product CO_2-pulse increased by fivefold over the course of the reduction. This increase in peak width can best be attributed to the increasing strength of adsorption at reduced sites on the catalyst surface.

(*d*) *Kinetic order.* A bimolecular disproportionation mechanism should exhibit a second order dependence on CHF_2Cl, at least at low surface coverages, if the halogen exchange reaction is the rate-determining step. As a test of this hypothesis, we examined the dependence of the rate of formation of CHF_2Cl reaction products on the integrated pulse intensity of the CHF_2Cl fed to the reactor over Cr_2O_3 which had been activated and equilibrated by treatment with CHF_2Cl at 698 K. As a measure of the reaction rate, the initial amount of CHF_3 formed (proportional to its rate of formation) *vs.* integrated CHF_2Cl pulse intensity was examined. A full composition measurement was carried out at each pulse intensity to insure an accurate measure of the CHF_3 composition. After applying a small linear correction to account for variations in average residence time in the reactor (resulting from a transition from Knudsen diffusion to viscous flow), the data was fitted to a simple non-integral power model. We found the order for the reaction (*c.f.* Appendix) to be 0.91 ± 0.06 indicating the absence of a bimolecular mechanism, if halogen exchange is the rate-determining step in this process. Figure 9 summarizes our findings.

DISCUSSION

The chrome oxides used in this study as catalysts for the disproportionation of CHF_2Cl apparently are required to undergo at least two separate surface transformations before becoming catalytically active. The first transformation involves a surface reduction as indicated by the oxidation of such reducing agents as CO and H_2 at elevated temperatures. This reaction of nominally Cr^{3+} oxides is not a new reaction hav-

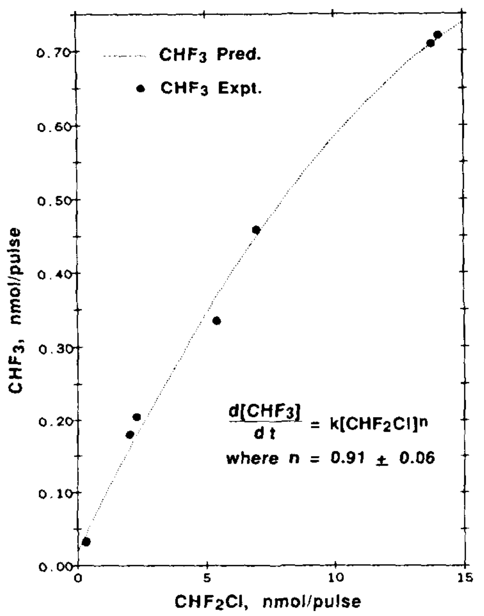

FIG. 9. CHF_2Cl reacting at various pulse intensities over Cr_2O_3 to yield CHF_3.

ing been observed by other workers investigating other catalytic reactions of these oxides (*14, 20, 25*) and related chromia/aluminas (*27, 28*). For example, Winfield *et al.* (*14*), have observed the reaction of chromia catalysts with hydrogen and ascribed this reaction to reduction of Cr^{4+} and Cr^{6+} surface sites. The oxidants are generally agreed to be high-valent Cr sites present on the surface of chromia-based catalysts. The resulting reduced sites are expected to be powerful Lewis acid sites since they should possess high positive charge densities resulting from the stripping of oxygen from the metal atoms by the reductants. This is borne out by the observed increase in Lewis acidity of these oxides upon reduction by CO, as measured by dimethyl ether temperature-programmed desorption. The second transformation appears to involve the reaction of these highly reactive reduced sites with an HCFC to yield halogenated metal sites. In addition, the surface Lewis acidity appears to undergo a further increase, as noted above, when CHF_3 was used as an activator.

The formation of the metal halide sites is implied by the formation of CO as the major reaction product during the initial stages of the reaction of CHF_2Cl with CO-reduced Cr_2O_3. Using ^{13}CO, the CO produced was also shown to not result from CO that might have been left behind from the CO reduction step. However, the absence of HF or HCl among the volatile products of the second transformation indicates that at least some of the halogen is present on the surface as complexed HF or HCl. The fact that hydrogen halides were observed as volatile products at higher temperatures suggests that these products were not irreversibly bound to the surface. Finally, our XPS results clearly indicate the presence of chromium fluorides on the surface of CHF_3-treated Cr_2O_3.

The valence states of the active chromium sites both prior to and following these transformations are not well defined. However, the formation of both Cr^{2+} and Cr^{+3} following the reduction of high-valent chrome oxide sites by CO is well documented for both α-Cr_2O_3 and α-Cr_2O_3/Al_2O_3 mixtures (*20, 27, 28*). Importantly, coordinatively unsaturated Cr^{2+} sites formed on Cr_2O_3/Al_2O_3 surfaces in this manner have been reported to be rapidly oxidized by O_2 or H_2O at ambient temperatures (*27, 28*). As noted above, the disproportionation reaction is not affected by the addition of oxygen, either prior to or during the feeding of CHF_2Cl to the catalyst at 323 K. Also, treatment of CO-reduced Cr_2O_3 with water at 698 K yielded a catalyst possessing *ca.* half the activity of an untreated control sample. The reduction in activity noted could have been the result of partial site blockage by adsorbed water. If Cr^{+2} sites are necessary for catalysis to occur, then no activity should have been observed in either case. Finally, CO, but no reduction products, such as H_2, H_2CO, or CHF_2CHF_2, were observed on reaction of CHF_2Cl with CO-reduced Cr_2O_3, indicating the CHF_2Cl is not reduced by the chromium surface. The well-known reducing properties of Cr^{2+} salts towards alkyl halides (*29*) would suggest that a rapid reduction of CHF_2Cl should occur under our reaction conditions if significant quantities of Cr^{2+} sites were present. No such reactions were observed. Thus, this lack of evidence for reduction products suggests that the valence state of chromium following the first transformation is probably largely Cr^{+3} and remains unchanged during the second transformation. Importantly, while Cr^{+2} may be present following the first transformation, it does not appear to be required for catalysis to occur. The initial valence state(s) of the chromium sites that are reduced during the first transformation is also uncertain. However, as noted above, the precursors to the active sites are *non-water-soluble* higher-valent Cr species. This could mean that these precursor sites are Cr^{4+} or Cr^{5+} sites and not Cr^{6+} sites, although non-soluble Cr^{6+} species are possible.

Our results lead us to propose coordinatively-unsaturated Cr^{3+} centers as necessary components of the active sites of the disproportionation reaction of CHF_2Cl over chrome oxides. In addition, we feel that these centers must contain Cr–X (X = F or Cl) bonds, leading to an enhancement of the Lewis acidity of these centers. While a detailed description of a mechanism is not possible from our data, the kinetic evidence does rule out a Rideal–Eley mechanism where a free organic species reacts with a surface-bound organic species in the rate-determining step. Unfortunately, a kinetic model corresponding to a monomolecular halogen-exchange reaction of HCFCs with metal halide sites, as given by our halogenated-site model, could not be tested due to the complexity of the model. However, evidence that the disproportionation of CHF_2Cl does not follow a bimolecular mechanism, where two CHF_2Cl molecules simultaneously exchange their halogens, comes from the TAP study showing the formation of varying ratios of the disproportionation products in the initial phases of the disproportionation. Finally, in preliminary studies, we have shown that the treatment of Cr_2O_3 with reducing agents acts to produce a catalyst active in the fluorination of CHF_2Cl with HF. Thus, the chromia sites responsible for HCFC disproportionation are very likely the same ones responsible for fluorination reactions of these materials.

APPENDIX

The determination of the kinetic orders of a reaction occurring during the passage of a pulse of reactant through a packed catalyst bed, as in the TAP reactor, may be carried out using a variety of explicit physical models (*30*). However, these models are sometimes difficult to apply in practice and approximate methods are often useful. An approximate model, applicable to the TAP reactor experiments described above, is described here which allows one to determine the order of a reaction in a reactant or product using a minimal set of data. This model shall be derived for the simple reaction,

$$A \rightarrow B, \qquad \text{(a)}$$

where A is a gaseous reactant and B a gaseous product. It is further assumed that the microscopic rate law for this reaction may be given by a power-law rate expression of the form

$$\text{Rate of formation of B} = k_r A(A_0, S_0, T, x, t, k)^n, \qquad \text{(b)}$$

where $A(A_0, S_0, T, x, t, k)$ represents the concentration of A along the reactor bed and where A_0 represents the initial concentration of A at the entrance to the bed and S_0, the surface concentration of active catalyst sites. The reaction rate constant is given by k_r. Temperature, T, time, t, axial position along the reactor, x, and various system rate constants, k, represents additional parameters (in an effort to minimize this cumbersome notation, only a limited variable set will be included in the formulas below). This model assumes that all parameters are independent of the radial coordinates.

A frequently-measured quantity in a typical TAP experiment is the quantity Q_B, the total amount of the material B formed following the passage of a pulse of A through the reactor. Q_B may be described by the expression

$$\begin{aligned} Q_B &= Q_{B_0} + \sigma \int_0^{t_p}\int_0^L (\mathit{Rate\ of\ reaction})\,dx\,dt \\ &= Q_{B_0} + \sigma \int_0^{t_p}\int_0^L k_r A(A_0, T, x, t)^n\,dx\,dt, \end{aligned} \tag{c}$$

where the reaction rate is integrated over the length, L, of the reactor and the time period, t_p, over which the measurements are taken. This time period is arbitrary but may be taken to be a time over which >99% of the reactant A has passed through the reactor. The quantity σ is the cross-sectional area of the reactor. The quantity Q_{B_0} is the initial quantity of B fed to the reactor.

Using Eq. (c) we may define expressions from which the kinetic order, n, of this process may be determined. In order to accomplish this, we need first to establish conditions under which the dependence of $A(A_0, T, x, t)$ on A_0 may be defined. While the form of the function $A(A_0, T, x, t)$ is unknown, we may expand this function as a power series in A_0 in order to quantify its dependence on A_0:

$$A(A_0, T, x, t) = \sum_{i=1}^{\infty} \alpha_i(T, x, t)\, A_0^i \tag{d}$$

As a first-order approximation, we may express A as the first term in the above series,

$$A(A_0, T, x, t) = \alpha_1(T, x, t)A_0, \quad \text{where } 0 \le \alpha_1(T, x, t) \le 1. \tag{e}$$

For an unreacting gas, at constant temperature, this approximation is equivalent to assuming that the average residence time of a gas passing through the reactor is independent of the amount of gas present. This turns out to be a good approximation when the partial pressure of the gas is low enough to be in the Knudsen flow regime since in this regime both experiment and theory show a virtual lack of dependence of average residence time on the quantity of gas present in a pulse (*21*). Even for partial pressures somewhat higher than this the approximation remains good, in our experience. However, when a gas is reacting, the dependence on A_0 must also include the effects of reaction. Obviously, when changes in $A(A_0, T, x, t)$ are small, due to low conversions of A to products, then eq. e should remain a good approximation. A special case, however, occurs when A reacts by a first-order process. In this case, any linear dependence of $A(A_0, T, x, t)$ on A_0 due to reaction is reinforced by the inherent linearity of A on A_0 in first-order processes. Thus, even at relatively high conversions of A, Eq. (e) probably remains a good approximation to A in this case.

Using the approximation given by Eq. (e), Eq. (c) becomes

$$Q_B = Q_{B_0} + \sigma A_0^n \int_0^{t_p}\int_0^L k_r \alpha_1(T, x, t)^n\,dx\,dt. \tag{f}$$

At low conversions of A to products, the integral in Eq. (f) remains relatively constant (at constant temperature) as A_0 is varied, with $\alpha_1(T, x, t)^n$ varying between zero and unity,

$$\begin{aligned} Q_B &= Q_{B_0} + \sigma A_0^n \int_0^{t_p}\int_0^L k_r \alpha_1(T, x, t)^n\,dx\,dt \\ &= Q_{B_0} - \sigma A_0^n F_1 \end{aligned} \tag{g}$$

$$\begin{aligned} n &= \frac{\ln(Q_{B_0} - Q_B) - \ln \sigma F_1}{\ln A_0} \\ &= \frac{\ln(Q_{B_0} - Q_B) - K}{\ln A_0}, \end{aligned} \tag{h}$$

where F_1 is the integral factor and K is a parameter determined by the experimental data. Thus, by simply varying A_0 and measuring Q_B, the order, n, of the reaction in A may be easily determined.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of J. Scott McCracken in performing TAP reactor experiments and Charles A. Bellini in carrying out the microreactor experiments. We thank P. L. Mills for helpful discussions regarding the interpretation of TAP reactor results. We also thank K. Kourtakis for preparing samples of the chromia catalysts used in this study. XPS studies were carried out by G. Blackman and J. Wyre. TGA-MS studies were carried out by M. J. Peterson.

REFERENCES

1. Bechadergue, D., Blanchard, M., and Canesson, P., *in* "Heterogeneous Catalysis and Fine Chemicals" (M. Guisnet *et al.*, Eds) p 257. Elsevier, Amsterdam, 1988.
2. Bechadergue, D., Blanchard, M., and Canesson, P., *Appl. Catal.* **20,** 179 (1986)
3. Hess, A., and Kemnitz, E., *Appl. Catal. A: General* **82,** 247 (1992).
4. Kolditz, L., Kauschka, G., and Schmidt, W., *Z. Anorg. Allg. Chem.* **434,** 41 (1977).
5. (a) Kolditz, L., Calov, U., Kauschka, G., and Schmidt, W., *Z. Anorg. Allg. Chem.* **434,** 55 (1977); (b) Kolditz L., Nitzche V., Heller G. and Stosser R., *Z. Anorg. Allg. Chem.* **476,** 23 (1981).
6. Okazaki, S., *Shokubai* **10** (4), 242 (1968).
7. Vecchio, M., Gropelli, G., and Tatlow, J. C., *J. Fluorine Chem.* **4,** 117 (1974).
8. Cavaterra, E., Fattore, V., and Giordano, N., *J. Catal.* **8,** 137 (1967).
9. Kemnitz, E., Hass, D., and Grimm, B., *Z. Anorg. Allg. Chem.* **589,** 228 (1990).
10. Kemnitz, E., Hass, D., Metzgen, W., Kohne, A., Noak, M., and Janchen, J., *Z. Phys. Chem.* **271,** 515 (1990).
11. Maragoni, L., Gervasutti, C., and Conte, L., *J. Fluorine Chem.* **19,** 21 (1981/82).
12. Kijowski, J., Webb, G., and Winfield, J. M., *J. Fluorine Chem.* **24,** 133 (1984).
13. Kijowski, J., Webb, G., and Winfield, J. M., *J. Fluorine Chem.* **27,** 213 (1985).
14. Kijowski, J., Webb, G., and Winfield, J. M., *Appl. Catal.* **27,** 181 (1986).
15. Rowley, L., Webb, G., Winfield, J. M., and McCulloch, A., *Appl. Catal.* **52,** 69 (1989).
16. Gambaretto, G. *Atti Dell Ist. Veneto Di Sci., Lett. ed Arti; Cl. Sci. Mat. Natur.* **126,** 367 (1967).
17. Yao, Y.-F. Y., *J. Phys. Chem.* **69,** (11), 3930 (1965).
18. (a) Kirby, R. E., Garwin, E. L., King, F. K., and Nyaiesh, A. R., *J. Appl. Phys.* **62** (4), 1400 (1987); (b) Feve, L., Fontaine, R., Arsene, J., Lenglet, M., and Caillat, R., *C.R. Acad. Sci. Paris Ser 2* **301** (10), 701 (1985).
19. (a) Gumprecht, W. H., Manzer, L. E., and Rao, V. N. M., U.S. Patent 4,843,181 (1989), assigned to E. I. du Pont de Nemours & Co; (b) Lerou, J. J., U.S. Patent 5,036,036 (1991) assigned to E. I. duPont de Nemours & Co.
20. Shelef, M., Otto, K., and Ghandi, H., *J. Catal.* **12,** 361 (1968).
21. Gleaves, J. T., Ebner, J. R., and Kuechler, T. C., *Catal. Rev.-Sci. Eng.* **30,** 43 (1989).
22. Chernyuk, G. P., *Zh. Prikl. Khim.* **54**(6), 1384–1388 (1981).
23. Okazaki, S., and Eriguchi, H., *Chem. Lett.*, 891 (1980).
24. Curry-Hyde, H. E., Musch, H., and Baiker, A., *Appl. Catal.* **65,** 211 (1990).
25. (a) Rao, S. R., Sandle, N. K., and Ramkrishna, V., *Indian J. Chem.* **6,** 36 (1968); (b) Rao, S. R., and Ramkrishna, V., *Indian J. Chem.* **4,** 43 (1966); (c) McDaniel, M. P., and Burwell, Jr., R. L., *J. Catal.* **36,** 394,404 (1975).
26. Eischens, R. E., and Selwood, P. W., *J. Am. Chem. Soc.* **69,** 1590 (1947).
27. Van Reijen, L. L., Sachtler, W. M. H., Cossee, P., and Brouwer, D. M., *in* "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," Vol. 2, p. 829. Wiley, New York, 1965.
28. Indovina, V., Cordischi, D., De Rossi, S., Ferrais, G., Ghiotti, G. and Chirino, A., *J. Mol. Catal.* **68,** 53 (1991).
29. Hanson, J. R., *Synthesis*, 1 (1974).
30. Furusawa, T., Suzuki, M., and Smith, J. M., *Catal. Rev.-Sci. Eng.* **13,** 43 (1976).