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Kinetics of the Fluorination/Chlorination of 1-Chloro-1,2,2,2-Tetrafluoroethane

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The kinetics of the catalytic fluorination and chlorination of 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124) by HF and HCl to give pentafluoroethane (HFC-125) and 1,1-dichloro-2,2,-trifluoroethane (HCFC-123), respectively, were examined in order to further define the mechanisms of these reactions. An HF-treated preparation of 2% $CoCl_2$ on Al_2O_3 was used as a catalyst. Reaction of deuterium-labeled HCFC-124 with HF or HCl showed the deuterium to be retained in both reactant and products, suggesting the absence of carbenoid or olefinic intermediates in these halogenations. Thermodynamic and thermokinetic properties of these halogenations were also determined in order to determine the extent of contributions of reverse reactions to the kinetics of these halogenations. Kinetic studies indicated that these halogenations are consistent with a classical Langmuir–Hinshelwood mechanism where both HX (X = F or Cl) and HCFC-124 are adsorbed on identical active sites of the catalyst in the rate-determining step. © 1993 Academic Press, Inc.

INTRODUCTION

Gas-phase fluorinations of chlorocarbons using hydrogen fluoride are important routes to industrially significant chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs). However, despite their importance, little is known concerning the mechanisms of these reactions. Previous studies (*1, 2*) of Cr_2O_3- and AlF_3-catalyzed fluorinations of chlorofluorocarbons by HF support mechanisms where surface-fluorinated species are the active fluorinating agents. Winfield and co-workers (*3*) have proposed that fluorinations of chlorofluroethanes proceed through the reaction of an adsorbed CFC with these surface-fluorinated species. Few kinetic studies of chlorocarbon fluorinations by HF have been reported. In early work, Gambaretto *et al.* (*4, 5*) examined the AlF_3-catalyzed fluorinations of CCl_4, $CHFCl_2$, and CFH_2Cl by HF and found the reactions to be first order in chlorocarbon and zero order in HF. However, the kinetic expressions which resulted from these studies were purely empirical, taking no account of the effects of the adsorptions/desorptions of the reaction components on the rates.

Gas-phase fluorinations of CFCs and HCFCs with HF have been reported (*6*) to be catalyzed by a variety of Lewis acid catalysts. Recently, a unique catalyst was reported (*7*) that selectively catalyzes the reaction of HF with perchloroethene to form mainly 1,2-dichloro-2,2,2-trifluoroethane (HCFC-123) and 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124), intermediates used in the commercial production of the alternative hydrofluorocarbon pentafluoroethane (HFC-125). This catalyst was prepared by HF treatment of $CoCl_2/Al_2O_3$ compositions and is designated here as Co/Al/F. As part of a study of this fluorination, we carried out a detailed study of the mechanism of the Co/Al/F-catalyzed fluorination of HCFC-124 to pentafluoroethane. In the course of this study we also examined the kinetics of the chlorination of HCFC-124 to 1,2-dichloro-2,2,2-trifluoroethane (HCFC-123). As shown in the following, the results of this study have implications for understanding

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the mechanisms of Lewis-acid-catalyzed halogenations of other CFCs and HCFCs.

EXPERIMENTAL

All of the reactions studied were carried out in an Inconel 6″ × ¼″ o.d. tubular microreactor holding 2.59 g of 25 to 30 mesh Co/Al/F as a catalyst. The reactor was heated by a fluidized silicon carbide bath maintained at temperatures ranging from 588 to 763 K by a resistance heater. Average temperature fluctuations at the external wall of the reactor held at fixed control settings were ±0.5 K. Gases were delivered to the reactor through ⅛″ 305 stainless steel tubing using Tylan mass flow controllers calibrated for the gases used. Hydrogen fluoride was fed as a gas from a cylinder maintained at 318 K using an oil bath. A separate mass flow controller was used to control the flow of the feed gas mixture through the reactor. The pressures inside the reactor were maintained at 1.1 atm (1 atm = 101.33 kPa) using a back-pressure regulator. A sampling valve and loop assembly were used to separately sample reactor feeds and offgases at any time during a reaction study. Organic reactants and products were analyzed using a Hewlett–Packard 5710A gas-liquid chromatograph equipped with a flame ionization detector and a 15′ × ⅛″ 5% Krytox on 60/80 Carbopak BHT column. Exit gases were scrubbed with aqueous 30% KOH prior to exposure to the external environment. Since the catalyst activity slowly declined with use, occasional regeneration with air at 698 K for 16 h was required to maintain a roughly constant activity level. Over time a slow, irreversible decline in activity was also noted. To correct for these changes in catalyst activity, a monitoring sample using a standard set of conditions was taken at the beginning of each day. The results of this activity monitoring were used to normalize the rates for small changes observed as a result of changes in catalyst activity. Finally, due to the observed slow equilibration of the reaction system following some feed composition changes, samples at a given compositoin were duplicated until the measured compositions of HFC-125 and HCFC-123 differed by less than 2% between runs. Thus, a minimum of two samples were taken for each feed composition. Usually, two or three samples were sufficient to obtain the desired data. Contact times (c/t) are defined as (catalyst volume)/(reactor gas flowrate at STP), where STP refers to standard temperature (273.15 K) and pressure (101.15 kPa). Mass spectra were measured on trapped gaseous samples using a Finnigan Model 4500 mass spectrometer.

The measurement of the isosteric heat of adsorption of HCFC-124 at ca. 1% of surface coverage on Co/Al/F was determined by a gravimetric technique using a Kahn microbalance. Differential weight changes accompanying exposure of the catalyst to varying partial pressures of HCFC-124 in nitrogen as a function of temperature were used to define the adsorption isotherms used in the calculations.

The gases HCFC-124 (99.9%), HF, HCl, and N_2 were used as received from commercial sources.

Catalyst Preparation

A sample of 2% $CoCl_2/Al_2O_3$ was prepared by impregnating 25–30 mesh Harshaw 3945 γ-alumina with an aqueous solution of cobalt chloride followed by drying at 423 K/1 h. This material was then treated with a stream of 50% hydrogen fluoride in nitrogen at 423 K for 2 h and finally at 698 K for 8 h. Examination of material resulting from several examples of his treatment was found to yield a material in which 85–98% of the oxygen was replaced by fluorine. The resulting light blue solid, designated here as Co/Al/F, was used directly in the reactor. A BET surface area measurement using N_2 as the adsorbing gas yielded a surface area of 26.9 m^2/g. Nitrogen adsorption mesurements yielded an average pore volume of 0.17 cc/g and an average pore radius of 12.1 nm. A recent report (*8*) describes the preparation and properties of a related series of fluorinated aluminas and their interactions with HCFCs.

Preparation of 1-Chloro-1-deuterio-1,2,2,2-tetrafluoroethane (DCFC-124)

The preparation of DCFC-124 was carried out by H/D exchange of HCFC-124 with D_2O using NaOD as a catalyst. In a typical preparation, a sample (25.0 g, 183 mmoles) of HCFC-124 was shaken with a solution of NaOD in D_2O (1.5 cc of 40 wt% NaOD in 36 cc of 99.5% D_2O) for 24 h at 373 K in a 240-cc stainless-steel cylinder under autogenous pressure. Mass spectral analysis of the resulting gas revealed a mixture containing 96% DCFC-124 and ca. 4% HCFC-124 along with traces of CF_2ClCDF_2, CF_3CDF_2 and $CF_2{=}CF_2$. ^{19}F NMR analysis revealed a new multiplet centered at −157.04 (relative to $CFCl_3$ in a solution of $CDCl_3$) assigned to the –CFDCl group shifted downfield by 0.57 ppm from –CFHCl.

HCl and HF Analysis

An electrochemical analysis technique was used to analyze for HF and HCl in the reactor offgases. In this technique a precise volume of offgas was sampled using a GLC sampling valve and loop (5 cc volume). The sample was then flushed with nitrogen through a heated (423–473 K) Inconel exit line to a sample vial containing 5 cc of a buffered solution of .20 *N* sodium acetate in 5.68×10^{-4} *N* acetic acid. Both the temperature and the electrochemical potential of the buffered solutions were measured, before and after sampling, using either a F or Cl ion-specific electrode. Using this information, the halide concentrations of the solutions were then calculated. In the case of chloride analysis, the resulting solutions were often less than 10^{-4} molar in Cl. Thus, we employed a modified-Nernst equation, based on a reported theoretical relationship (9) for AgCl electrodes, to account for the non-linearity of the electropotential as a function of $\log[Cl^-]$ at these concentrations. The analysis for HF was carried out using the well-known Nernst equation to relate electrochemical potential to fluoride concentration. Both techniques measured halide concentrations with average precisions of ca. 3 to 4%.

RESULTS

Reaction Conditions and Products

The catalytic fluorination of HCFC-124 by excess HF proceeded smoothly at temperatures between 573 and 673 K to yield HFC-125:

$$CF_3CHFCl + HF \rightarrow CF_3CHF_2 + HCl. \quad (1)$$

At the percent conversion levels studied here (<13%), small quantities of CF_3CHCl_2 (HCFC-123) and lesser quantities of $CF_2ClCHFCl$ (HCFC-123a) and CF_3CH_2Cl (HCFC-133a) were also usually coproduced. These materials together constituted less than ca. 3% of the products formed. The HCFC-123 and HCFC-123a presumably arose from the competing chlorination of HCFC-124 by the coproduced HCl. The formation of HCFC-133a was a minor reduction product usually present in amounts of less than 0.5% of the converted HCFC-124. Overall, a good material balance was achieved with negligible amounts of nonvolatile carbonaceous materials formed. At higher conversions and/or lower HF : HCFC-124 ratios, competing chlorination reactions became increasingly important resulting in the formation of small amounts of $CF_2ClCHCl_2$ (HCFC-122), $CFCl{=}CCl_2$ (HCFC-1111), and $CCl_2{=}CCl_2$ (HCFC-1110). For unknown reasons, the formation of these products was usually associated with shortened catalyst lifetimes due to the deposition of carbonaceous materials on the catalyst.

Fluorination of 1-Chloro-1-deuterio-1,2,2,2-tetrafluoroethane (DCFC-124)

The reaction of DCFC-124 with HF was studied to determine the fate of the deuterium label. A mixture of DCFC-124 (containing 94.2% D) and HF were passed over

TABLE 1

Product Distribution Resulting from Fluorination/Chlorination of 1-Chloro-1-deuterio-1,2,2,2-tetrafluoroethane (DCFC-124)[a]

	% Composition (% D)		
Compound	HFC-125	HCFC-124	HCFC-123
Feed	0.03 (93.9)	8.17 (94.2)	<0.01
Product	1.94 (94.3)	6.85 (93.4)	0.088 (93.4)

[a] Reaction conditions are HF : HCFC-124 = 10.5, c/t = 24 s, pressure = 1.08 atm, and temp. = 648 K.

Co/Al/F at 648 K. A gas sample was analyzed using mass spectroscopy to give the %D contents of the organic reactant and products shown in Table 1. Within the errors of the measurements, complete retention of deuterium was observed in both the fluorination and chlorination products of DCFC-124. In addition, no exchange of the deuterium in DCFC-124 with the hydrogen in HF was noted.

Thermodynamics and Thermokinetics of Halogenation

Prior to beginning the kinetic study, the thermodynamic properties of these halogenations were determined. This was done primarily to enable a calculation of the contributions of reverse reactions to the reactions being studied. Using this information, we were able to define the extent to which reverse rections would affect the corresponding forward reactions at the levels of conversion selected for this study. Because of the complexity of the kinetic expressions describing these reactions, it was necessary to restrict our study to those conditions where the contributions of the reverse reactions could be neglected.

Since experimental values for the thermodynamic properties associated with these halogenations were not available, we decided to calculate these quantities using the thermodynamic property values of the individual reactants and products. Using property values reported for HF (*10*), HCl (*10*), and HCFC-125 (*11*) and calculated for HCFC-124 and HCFC-123, using an ab initio molecular orbital method (*12*), we were able to determine gas-phase thermodynamic property values for these halogenations. The values found are given in Table 2.

As a check on these calculations and as a verification of the absence of mass transfer effects affecting the kinetics, we also measured the Arrhenius activation energies associated with each of the halogenation reactions. The Arrhenius activation energies of each of the halogenation reactions of HCFC-124 and the corresponding reverse reactions were measured using the well-known method of measuring the variation of initial rates as functions of temperature. During these measurements, the HF : HCl : HCFC (or HFC) reactant ratios were maintained at the constant values of 7.2 : 7.2 : 1.0 (for the HCFC-124/HFC-125 system) and 6.0 : 6.0 : 1.0 (for the HCFC-

TABLE 2

Thermodynamic Parameter Values for the Fluorination/Chlorination of 1-Chloro-1,2,2,2-tetrafluorethane (HCFC-124)[a]

Equilibrium	Heat of reaction (kJ/mol)[b]	Entropy of reaction (J/mol K)[b]
$CF_3CHFCl + HF \rightleftharpoons CF_3CHF_2 + HCl$	−10.5 (6.3)	2.1 (2.9)
$CF_3CHFCl + HCl \rightleftharpoons CF_3CHCl_2 + HF$	−1.7 (5.9)	−5.0 (2.9)

[a] Gas-phase properties defined for 298 K and 1 atm pressure.

[b] Errors, in parentheses, represent estimated 2 standard errors.

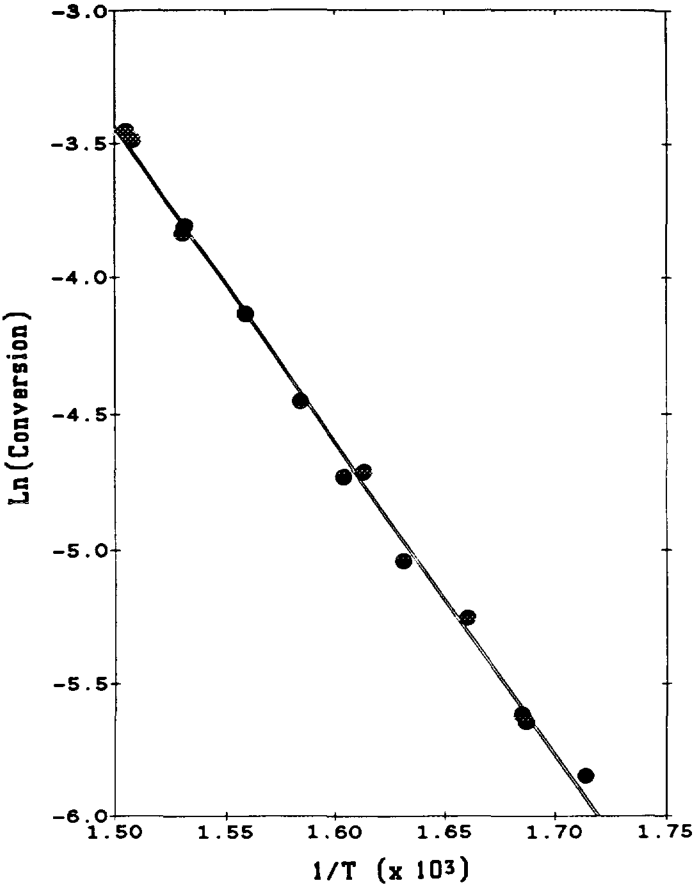

FIG. 1. Arrhenius plot for reaction of HCFC-124 with HF to form HFC-125. HF : HCl : HCFC-124 = 7.2 : 7.2 : 1.0; c/t = 4.7 s.

124/HCFC-123 system) (*13*) and the % conversions of each of the HCFC reactants were kept to values at or below 10%. As a result of the presence of comparable amounts of both HF and HCl in a given feed, fluorinations and chlorinations were observed simultaneously. The activation energies were then determined from the classical Arrhenius relationship by assuming that the initial rates represented pseudo-zero-order rate constants, since all reagent concentrations remained relatively constant throughout these determinations. Figure 1 is an example of a typical Arrhenius plot found for the reaction of HCFC-124 with HF. Table 3 documents the activation energies found for each reaction. The resulting activation energies were used to calculate the *apparent* heats of reaction, ΔH_{app}, for each reaction also given in Table 3. Since a relationship exists (*14*) between Arrhenius activation energies, E_f and E_r, for the forward and reverse reactions of an equilibrium and the actual heat of reaction of these halogenations, a calculation of the latter quantity was considered feasible. This relationship, however, depends upon knowing the stoichiometric number, σ, associated with a given reaction:

$$E_f - E_r = \Delta H_{\text{app}} = \frac{\Delta H_r}{\sigma}. \quad (2)$$

Using this relationship, we attempted to de-

TABLE 3

Arrhenius Activation Energies and Heats of Reaction for the Fluorination/Chlorination of 1-Chloro-1,2,2,2-tetrafluorethane

Equilibrium	T range (K)	Reaction	E_{act} (kJ/mol)[a]
$CF_3CHFCl + HF \rightleftharpoons CF_3CHF_2 + HCl$	583–664	Forward	96.7 (3.6)
	693–763	Reverse	107.7 (7.8)
			ΔH_{app} = −11.0 (8.4)
$CF_3CHFCl + HCl \rightleftharpoons CF_3CHCl_2 + HF$	611–683	Forward	105.3 (3.2)
	621–693	Reverse	116.5 (2.2)
			ΔH_{app} = −11.2 (4.0)

[a] Errors, in parentheses, equal 2 standard errors.

termine the stoichiometric number associated with the fluorination/chlorination reactions examined here. However, the errors associated with both the calculated and measured heats of reaction were found to either approach or exceed the values themselves. Thus, definite values for the stoichiometric numbers could not be obtained. Nevertheless, using either the calculated or measured thermodynamic property values, we were able to conclude that the reaction conditions chosen for the study of the halogenation of HCFC-124 allowed us to assume that the corresponding reverse reactions would not slow the actual forward rates by more than ca. 3%. In addition, the finding that the reactions are only slightly exothermic led us to conclude that heat transfer processes within the reactor should have an insignificant effect on the reaction kinetics, especially at the low conversions studied here. Approximate heat transfer calculations supported this hypothesis. Finally, since the activation energies for these reactions gave excellent linear fits of the data over the temperature and concentration ranges studied here, we concluded that both reactor heat and mass transfer limitations on the rates were probably minimal.

Kinetics of Fluorination/Chlorination

Prior to a fully developed kinetic study, we chose to examine the reaction of HCFC-124 with HF and HCl under conditions where the partial pressures of each component were varied separately, keeping the partial pressures of all remaining reactants constant. These partial pressures were kept constant by the compensating addition of 20% CH_4 in N_2 feed, with the CH_4 serving as a marker for the N_2. In addition, runs where the total partial pressures of reactants, at constant ratios, were varied with the total system pressure held constant were also carried out. This latter set of runs was carried out by simply varying the relative flowrates of the 20% CH_4/N_2 feed with the remaining flowrates held constant. This technique was used to gain qualitative and semiquantitative information regarding the kinetic form of the reactions prior to measuring the actual parameter values.

The reactions in this phase of the study were carried out at 1.1 atm (1 atm = 101.33 kPa) total pressure and temperatures of 588 to 633 K. HCFC-124, HF, HCl, and 20% CH_4/N_2 were independently fed to the reactor. The initial rates of formation of HCFC-123 and HFC-125, as functions of individual variations in the partial pressures of each of the components, were first determined. Since the reactions were carried out at low conversions ($\leq$13%) of the limiting reagents, the rates of the reactions were calculated by assuming the reactor operated in the differential mode of an idealized plug flow reactor (*15*). Only the temperatures were varied in order to achieve the desired

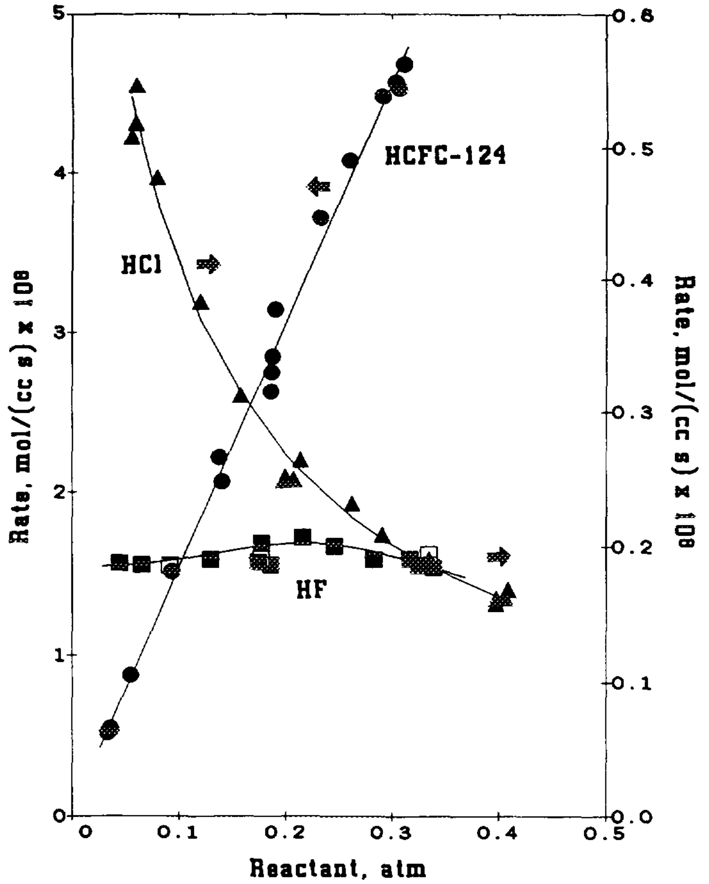

FIG. 2. Variation of rate reaction of HCFC-124 with HF as functions of HF, HCl, and HCFC-124 partial pressures. For HF, HCl : N_2/CH_4 + HF : HCFC-124 = 1.23 : 1.05 : 1.00; T = 583 K; c/t = 3.7 s. For HCl, HF : N_2/CH_4 + HCl : HCFC-124 = 1.10 : 1.33 : 1.00; T = 580 K; c/t = 3.7 s. For HCFC-124, HF : HCl : CH_4/N_2 + HCFC-124 = 1.40 : 0.48 : 1.00; T = 651 K; c/t = 3.0 s.

conversions. Examples of the results obtained are given in Figs. 2 and 3. These figures display the effects on the rate of formation of HFC-125 as a result of separately varying the partial pressure of HCHC-124, HF, HCl, and of all reactant components simultaneously, respectively. Similar results were found for the rates of formation of HCFC-123 as functions of reagent partial pressures.

In a final preliminary study we also measured the isosteric heat of adsorption of HCFC-124 on Co/Al/F. Measurements were taken over a temperature range of 308 to 338 K, yielding an isosteric heat of adsorption of 25.9 kJ/mol at ca. 1% of surface coverage.

With the results from this preliminary study serving as a guide, we next carried out the reactions under conditions that would allow us to measure the kinetic parameters of the fluorination and chlorination of HCFC-124 over a wide range of compositions. The reactor offgases were analyzed for organics and HCl. In this case, the HF content of the offgases was not determined directly but was analyzed indirectly by measuring the CH_4 content of the mixtures. For a given day's set of samples, the HF was fed to the reactor along with 20% CH_4 in N_2

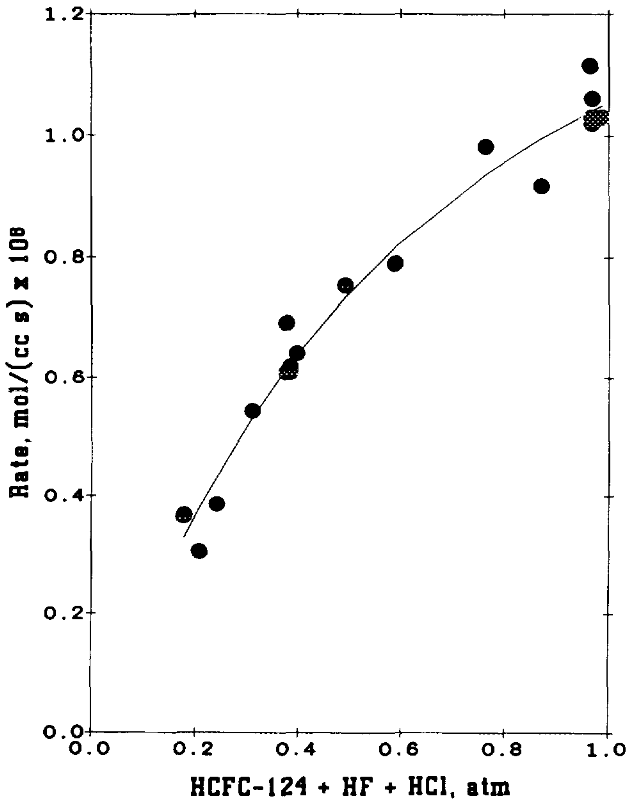

FIG. 3. Variation of rate of reaction of HCFC-124 with HF as function of total reagent partial pressures. HF : HCl : HCFC-124 = 10.1 : 1.98–1.00; T = 633 K; c/t = 1.38 s.

at a predetermined constant HF/CH_4 ratio. Thus, measurement of the CH_4 content of the gas streams, along with corrections based on reaction stoichiometry, permitted a calculation of the total HF present in the offgases. Actual measurements of HF, using our electrochemical technique, verified the accuracy of this method. The input feeds were composed of various compositions containing HF, HCl, HCFC-124, and 20% CH_4/N_2, each independently fed.

Running in differential mode (<10% conversion), the initial rates of reaction found for HCFC-124 reacting with various partial pressures of HF and HCl, were measured, using a modified block design (*16*), at 633 K. Under some conditions, e.g., high partial pressures of HCl, small amounts of HCFC-123 chlorination products were observed. The rates of formation of these products were added to the rates of formation of HCFC-123 in the data. The rates of formation of HCFC-123a were also included as part of the rates of formation of HCFC-123. A total of 32 product compositions, 13 of which were replicates, were analyzed.

Analysis of the reaction data was initially carried out by comparing the rates found with those predicted by several Langmuir–Hinshelwood (L–H) models (cf. Table 4). The data was first normalized to correct for changes in catalyst activity. The rates were compared using a weighted, nonlinear regression procedure written to carry out a statistical analysis of the data along with a determination of the rate parameter values. The weighting procedure used in this study involved the weighting of each data

TABLE 4

Kinetic Models of the Rates of Fluorination/Chlorination of 1-Chloro-1,2,2,2-tetrafluorethane (HCFC-124)[a]

Model	Kinetic terms		Adsorption term	Rate-determining step[c]
	Fluorination	Chlorination		
1[b]	$k_2K_1P_{124}P_{HF}$	$k_3P_{124}P_{HCl}$	$P_{HCl} + K_1P_{HF}$	R_F–X + S–Y → R_F–Y + S–X
2[b]	$k_4K_1K_2P_{124}P_{HF}$	$k_5K_3P_{124}P_{HCl}$	$(P_{HF}(K_1K_2K_7P_{HF} + K_1K_3P_{HCl}(1 + K_2) + K_1K_2) + P_{HCl}(K_3K_6P_{HCl} + K_3))$	R_F–X + S–Y → R_F–Y + S–X
3	$k_2K_1P_{124}P_{HF}$	$k_4K_3P_{124}P_{HCl}$	$1 + K_3P_{HCl} + K_1P_{HF}$	R_F–X*S + HY → R_F–Y*S + HX
4	$k_3K_1K_2P_{124}P_{HF}$	$k_5K_1K_4P_{124}P_{HCl}$	$(1 + K_1P_{124} + K_4P_{HCl} + K_2P_{HF})^2$	R_F–X*S + HY*S → R_F–Y*S + HX*S
5	$k_3K_1K_2P_{124}P_{HF}$	$k_5K_1K_7P_{124}P_{HCl}$	$(1 + K_1P_{124}) * (1 + K_7P_{HCl} + K_2P_{HF})$	R_F–X*S_1 + HY*S_2 → R_F–Y*S_1 + HX*S_2

[a] The terms corresponding to Langmuir–Hinshelwood rate expressions are given as a kinetic term divided by an adsorption term. Upper case K's represent equilibrium constants, while lower case k's represent rate constants.

[b] Site-halogenated species may be formed from S–OH + HX = S–X + H_2O, where X is F or Cl.

[c] In fluorination X = Cl, Y = F, while for chlorination X = F, Y = Cl.

point by the square root of the reciprocal of its variance. The variance of each data point was derived from the measured variances of a select set of runs using a linear regression procedure to estimate the variances of the remaining data points. The resulting parameter values and statistical analyses associated with five basic models are described in Table 5 for the separate rates of formation of HCFC-123 and HFC-125.

In Table 5 the quantity "F-ratio" is used to measure the degree of fit of the data to each given model. The quantity "F-ratio" is the familiar ratio of the mean squares of the lack-of-fit residual to that of the pure error residual resulting from a nonlinear least squares minimization procedure (*17*). In the case of the nonlinear models studied here, this ratio should be viewed as a useful, but approximate, measure of the degree of fit of the data to a given model. However, it may be noted from Table 5 that one of the models gave *negative* F-ratios. The reason for this anomaly lies in the assumptions inherent in the statistical procedure. This procedure assumes that sets of *exact* repeats of process conditions exist in the data set. Unfortunately, we were not able, in most cases, to precisely replicate previous feed compositions. Thus, while the resulting product compositions could be accurately measured, they represented only approximate replicates of previous runs. This replication problem led to increases in the pure error terms beyond that actually due to the errors in the rate measurements. The result is F-ratios that are abnormally low. However, the *relative* F-ratio values may be used to guide a choice of models. Examination of Table 5 reveals that both rates were best modeled (possess the smallest F-ratio) by a model where, in the rate-determining step, both the HCFC and the HX coreactant are competitively adsorbed on identical active sites (Model 4 in Table 4). Also, the weighted residuals associated with this model did not show any systematic behavior that would suggest an incorrect model. This model is termed the "identical double-site model." Additional reasons for selecting this model over the others considered are presented in the Discussion. A brief description of the identical double-site model along with the definition of accompanying equilibrium and rate constants is given below (S is an undefined active site with "*" denoting physi- or chemisorption of a species to this site):

TABLE 5

Fluorination/Chlorination Model Parameter Values[a]

Model	K	Fluorination (std. dev.)		Chlorination (std. dev.)	
		Parameter values	F-ratio	Parameter values	F-ratio
1	K_1	4.1 (1.8)	0.22	2.4×10^3 (2.1×10^4)	1.1
	k_2	0.38 (0.038)		—	
	k_3	—		4.0×10^3 (3.6×10^4)	
2	K_1	1.4×10^2 (3.1×10^2)	25.9	20 (1.8×10^2)	480
	K_2	-1.4×10^{-1} (1.2)		1.6 (26)	
	K_3	15 (1.4×10^2)		22 (2.0×10^2)	
	k_4	-9.6×10^{-1} (2.5)		—	
	k_5	—		2.8 (37)	
	K_6	−46 (91)		−5.0 (8.8×10^{-1})	
	K_7	25 (66)		−24 (1.3×10^2)	
3	K_1	5.2×10^6 (1.9×10^8)	0.24	3.5×10^6 (4.5×10^7)	1.1
	k_2	0.38 (0.039)		—	
	K_3	1.3×10^6 (4.7×10^7)		2.0×10^4 (3.2×10^5)	
	k_4	—		3.0×10^2 (2.7×10^3)	
4	K_1	6.4×10^{-4} (2.5×10^{-3})	−0.81	3.1×10^{-4} (3.0×10^{-3})	0.24
	K_2	12 (7.7×10^{-1})		19 (4.8)	
	k_3	3.0×10^3 (1.2×10^4)		—	
	K_4	3.5 (4.7×10^{-1})		2.4 (1.1)	
	k_5	—		3.2×10^5 (3.1×10^6)	
5	K_1	1.5×10^{-2} (2.5×10^{-1})	3.9	5.6×10^{-4} (2.0×10^{-2})	81
	K_2	1.6×10^5 (75.7×10^6)		−2.7 (2.2×10^{-1})	
	k_3	27 (2.7×10^2)		—	
	k_5	—		2.1×10^8 (4.9×10^9)	
	K_7	5.4×10^4 (2.0×10^6)		1.8×10^{-4} (4.5×10^{-3})	

[a] Refer to Table 4 for model description. Adsorption equilibrium constants are given in units of 10^{-2} atm^{-1}. Rate constants are given in units of mol/cc s $(\times 10^8)$.

(a) $\text{HCFC-124} + \text{S} \rightleftharpoons \text{HCFC-124*S}$ $\quad K_1 = k_1/k_{-1}$

(b) $\text{HF} + \text{S} \rightleftharpoons \text{HF*S}$ $\quad K_2 = k_2/k_{-2}$

(c) $\text{HCFC-124*S} + \text{HF*S} \longrightarrow \text{HFC-125*S} + \text{HCl*S}$ $\quad k_3$

(d) $\text{HCl} + \text{S} \rightleftharpoons \text{HCL*S}$ $\quad K_4 = k_4/k_{-4}$

(e) $\text{HCFC-124*S} + \text{HCl*S} \longrightarrow \text{HCFC-123*S} + \text{HF*S}$ $\quad k_5$

(f) $\text{HCFC-123*S} \rightleftharpoons \text{HCFC-123} + \text{S}$ $\quad K_6 = k_{-6}/k_6$

(g) $\text{HFC-125*S} \rightleftharpoons \text{HFC-125} + \text{S}$ $\quad K_7 = k_{-7}/k_7.$

When steps (c) and (e) are the rate-determining steps, the rates of formation of HFC-125, R_{125}, and HCFC-123, R_{123}, take the forms

$$R_{125} = \frac{k_3 K_1 K_2 P_{124} P_{\text{HF}}}{(1 + K_1 P_{124} + K_4 P_{\text{HCl}} + K_2 P_{\text{HF}} + K_6 P_{123} + K_7 P_{125})^2} \tag{3}$$

$$R_{123} = \frac{k_5 K_1 K_4 P_{124} P_{\text{HCl}}}{(1 + K_1 P_{124} + K_4 P_{\text{HCl}} + K_2 P_{\text{HF}} + K_6 P_{123} + K_7 P_{125})^2}, \tag{4}$$

where P_n represents the partial pressure of the reaction component n. Note that both HFC-125 and HCFC-123 appear in the denominator of these expressions. Based on

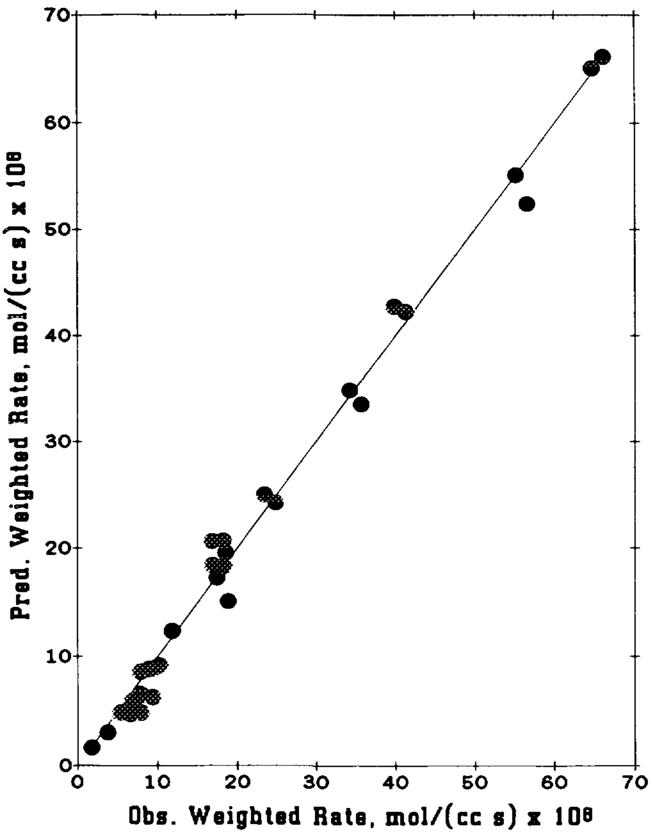

FIG. 4. Predicted vs observed rate of formation of HFC-125 for identical double-site model.

our previous finding that HCFC-124 appears to be only weakly adsorbed on this catalyst coupled with the low partial pressures of HFC-125 and HCFC-123 relative to HCFC-124, we have assumed the product adsorption contributions to be negligible in all models and have ignored their contributions to these expressions. The order found for the magnitudes of the K values ($K_2 > K_4 > K_1$) in the identical double-site model is also consistent with the ordering of the extents of the component adsorptions as HF > HCl > F-124, as previously implied from our partial pressure variation study. Interestingly, the intrinsic chlorination rate constant, k_5, in this model is ca. 100 times larger than that for fluorination, k_3. Apparently, the primary reason that chlorination products do not assume an even larger fraction of the products is due to the presence of a high surface concentration of HF relative to that of HCl. Figures 4 and 5 give the fits observed for the preferred L–H models for both reactions. The rates plotted in these figures are the normal rates multiplied by the reciprocals of the square roots of their predicted variances. The poorer fit observed for the chlorination model, compared to the fluorination model, may be explained by the relatively larger experimental error associated with the measurement of HCl compared to that of HF. In the fluorination model, experimental errors due to HCl measurements were found to have a relatively minor effect on the measured rate.

Attempts were made to measure the temperature dependence of the model parameters. However, despite extensive attempts, optimal values for the frequency factors and activation or adsorption energies associated with each of the Ks could not be found using the above-described weighted, nonlinear re-

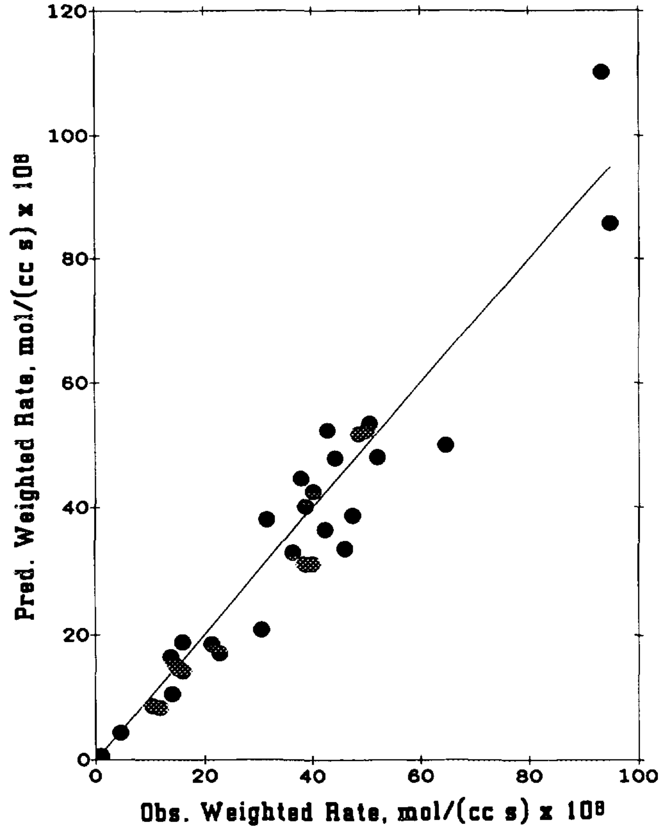

FIG. 5. Predicted vs observed rate of formation of HCFC-123 identical double-site model.

gression procedure. A proliferation of parameters (eight) coupled with a narrow accessible temperature range (588–663 K) resulted in parameter values possessing extremely large standard deviations.

DISCUSSION

The finding that DCFC-124 reacts with HF and HCl to yield halogenation products where the deuterium is essentially 100% retained in both the products and starting material supports mechanisms where deuterium (or hydrogen, in the case of HCFC-124) remains attached to carbon throughout the reactions. This finding also allows us to eliminate certain mechanisms from consideration. Thus, mechanisms involving intermediate carbenoid species resulting from HX elimination, e.g.,

$$CF_3CHFCl + S \xrightarrow{-HCl} [CF_3CF{=}S] \xrightarrow{HF} CF_3CHF_2 + S, \quad (5)$$

are unlikely. Olefinic species such as $CF_2{=}CFCl$ are also unlikely to be intermediates in these reactions.

The results of varying the partial pressures of single (and all) reaction components during reaction yielded the following conclusions.

(*A*) *The fluorination/chlorination reactions involve active sites where at least two adsorbed species are involved in the rate-determining step.* This follows from the form of the rate dependencies on the total partial pressures of the reactants (cf. Fig. 3). A linear dependence of the rate on total pressure is predicted for all of the L–H mechanisms examined here where only one adsorbed species is involved in the halogenation. The observation of significant curvature in this rate dependence suggests the presence of quadratic, or higher, order terms in the denominator of an L–H expression implying the involvement of more than one adsorbed species in the rate-determining step.

(*B*) *Assuming that HF is adsorbed on the catalyst active sites, it must be strongly adsorbed.* The finding of a near-zero-order dependence for the rate of formation of HFC-125 on HF (cf. Fig. 2), at comparable concentrations of HCFC-124, HCl and HF, implies a value for the HF adsorption constant that is larger than any of the other adsorption constants in the denominator of an L–H rate expression.

(*C*) *Assuming that HCFC-124 is adsorbed it must be weakly adsorbed, relative to HF or HCl, on the catalyst active sites.* This follows from the observance of a near-linear dependence of the rate of formation of HFC-125 on HCFC-124 (cf. Fig. 2). In addition, the measured isosteric heat of adsorption of HCFC-124 on the catalyst was found to be of a magnitude (25.9 kJ/mol) expected for a weakly-adsorbing substance. These considerations suggest that any terms involving HCFC-124 in the denominators of an L–H expression are almost negligible in comparison to the other terms. Because of structural similarities, it is also implied that HCFC-123 and HFC-125 are likely to be weakly adsorbed on the catalyst.

While these considerations limited the number of possible mechanisms followed by this chemistry, there still remained a sizable number of permissible mechanisms. The results of the detailed kinetic study allowed us to further reduce the number of likely mechanisms. Consideration of the *F*-ratios resulting from the fit of the data to the models and the internal consistency of the resulting adsorption constants allowed us to reject all but one of the models examined. In this manner, we were able to show that mechanisms *not* involving the elements of HX in the rate-determining step may be considered unlikely. Direct halogen exchange reactions, such as featured in the rate-determining steps of Models 1 and 2 of Table 4, are examples of such mechanisms. Both of these models were found to be deficient. While the *F*-ratio for Model 2 was sufficiently high to reject it out of hand, that for Model 1 was quite low. This latter model was, however, rejected on the basis of the inconsistency between the theoretically identical HF adsorption constants (K_1) found for the two reactions. A different mechanism involving the adsorption of HCFC and HX species on different sites (Model 5) was rejected on the basis of the poor fit given by the model to the data (as well as the prediction of negative adsorption constants). Finally, Model 3, an Eley–Rideal model involving attack of free HX on complexed HCFC, was also rejected on the basis of a poor model fit as well as an observed significant difference between the HCl adsorption constants (K_3) for the two halogenation reactions.

Of all the models studied, the identical double-site model (Model 4) appeared to give the best fit to the data. This model is attractive for two additional reasons. First, the two halogenations described by this model show a self-consistency not shown by the other models. This self-consistency may be seen by comparing the values of K_1, K_2, and K_4 (the surface adsorption constants of HCFC-124, HF, and HCl, respectively) given by the two rate expressions. The L–H model predicts the two rate forms to give equal values to these sets of parameters. Reasonable agreement between the two set of values is seen by noting that the values for the two rate forms are within two standard deviations of one another (cf. Table 5). Second, the identical double-site model is consistent with the findings of Winfield and coworkers (*1*), who suggested that a stable, surface-hydrohalogenated species could be the active halogenating agent in reactions of chlorofluorocarbons with HX. In our model the HX species may chemisorb on surface sites, prior to their reaction with the HCFCs, forming a stable surface-hydrohalogenated species. Permissible surface-hydrohalogenated species include Lewis acid complexes (S*HX) or metal hydrido halides (H–S–X) (where S is either a Lewis acid site or a low-valent metal site, respectively).

In addition to the models described in Table 4, another set of models was examined where the rate-determining steps were reactions involving the formation of active-site-HCFC complexes. None of these models were found to give good data fits since all of them predicted that the rates of formation of HCFC-123 and HCFC-125 should display a constant proportionality under the various conditions studied. This, of course, was not observed experimentally. Finally, while other possible halogenation models exist, our study was, of course, limited to those models that we could resonably distinguish from one another on the basis of our experimental data. The experimental errors inherent in our procedures limited us to models that did not contain more than about six independent parameters.

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