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HALOGEN EXCHANGE EQUILIBRIA OF CHLOROFLUOROOLEFINS

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SUMMARY

The thermochemical properties of the following reactions were determined using either AlF_3 or Cr_2O_3 as catalysts:

$$2\ CF_3CF{=}CFCl \xrightleftharpoons{200\text{-}300°C} CF_3CF{=}CF_2 + CF_3CF{=}CCl_2 \qquad (1)$$

$$2\ CF_3CCl{=}CFCl \xrightleftharpoons{350\text{-}450°} CF_3CCl{=}CF_2 + CF_3CCl{=}CCl_2 \qquad (2)$$

$$\begin{aligned}2\ CF_3CF{=}CF_2 + 2\ CF_3CCl{=}CCl_2 \xrightleftharpoons{225\text{-}350°} & CF_3CCl{=}CF_2 + CF_3CF{=}CCl_2 \qquad (3)\\ & + CF_3CCl{=}CFCl + CF_3CCl{=}CF_2\end{aligned}$$

In addition, the cis-trans equilibria of both $CF_3CF{=}CFCl$ and $CF_3CCl{=}CFCl$ were able to be derived from the reaction data. The experimental thermochemical properties for reactions (1), (2) and (3) were compared with property values calculated using a well-known approximation method.

A study of the exchange equilibria of chlorofluoroethylenes failed to yield accurate thermochemical values due to significant side reactions. However, a brief study of the mechanism of a catalytic disproportionation of $CF_2{=}CFCl$:

$$CF_2{=}CFCl \xrightarrow{Cr_2O_3} CF_2{=}CF_2 + CF_2{=}CCl_2 + CFCl{=}CFCl$$

was carried out.

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INTRODUCTION

It was recently reported[1] that chlorofluoroolefins of the general structure $R_FCX{=}CFCl$ (X = F, Cl; $R_F = CF_3$, F) readily undergo facile disproportionation reactions in the presence of certain metal oxide catalysts:

$$2\ R_FCX{=}CFCl \rightleftharpoons R_FCX{=}CF_2 + R_FCX{=}CCl_2$$

The efficiency of this catalysis combined with the dearth [2] of literature data measuring equilibria among fluoroolefins prompted us to examine the thermochemical properties of these reactions.

RESULTS AND DISCUSSION

Chlorofluoropropylenes

The thermochemical properties of reactions (1), (2) and (3), as shown in the Summary, were determined using either AlF_3 or Cr_2O_3 as catalysts.

Equilibrium (3) is actually a composite of equilibria (1), (2) and a third, independent equilibrium:

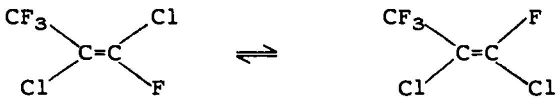
$$CF_3CF{=}CFCl + CF_3Cl{=}CFCl \rightleftharpoons CF_3CF{=}CF_2 + CF_3CCl{=}CCl_2 \qquad (4)$$

Thus, determination of the thermochemical properties of equilibria (1)-(3) allowed us to derive those of equilibrium (4) from simple additivity relationships. The thermochemical parameter values for these equilibria are summarized in Table 1. Tables 2, 3 and 4 describe the equilibrium compositions found for each of these reactions over the temperature ranges noted. Note that equilibria (1) and (2) involve halogen exchange at only the terminal carbons. No interchange of 2-halogen substituents was observed for these equilibria under reaction conditions. This strongly suggests that the reaction pathway for achieving equilibrium (4) also involves only terminal-carbon halogen exchange. The three equilibria represented by (1), (2) and (4), in fact, define all of the necessary independent reactions needed to relate these compounds through terminal halogen exchanges. Further evidence supporting the absence of 2-halogen exchange was found in our failure to effect an isomerization of 2-chloro-1,1,1,3,3-pentafluoro-2-propylene:

$$CF_3CCl=CF_2 \not\rightarrow CF_3CF=CFCl \qquad (5)$$

At 350°C a slow reaction ensued over Cr_2O_3 producing $CF_3CCl=CFCl$ and lesser amounts of various saturated chlorofluoro propylenes. All of the products contained a 2-chloro substituent. Since the product Cl:F ratio was higher than that of $CF_3CCl=CF_2$, additional, undetected products were presumably formed.

The presence of olefinic cis-trans isomers among the products of these disproportionations afforded us the rare opportunity to examine the thermochemistry associated with cis-trans isomerizations of chlorofluoroolefins. The



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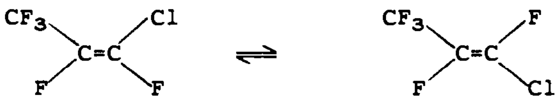


(7)

thermochemical properties of these equilibria are also included in Table 1. As expected, the trans isomers are favored, though not by a large amount. In addition, the relative steric effect of F vs. Cl shows up as a barely significant increase in the heat of reaction on going from a 2-F to a 2-Cl substituent.

TABLE 1

Thermochemical Property Values for Chlorofluoropropylene Exchange Equilibria[a]

Reaction	T, °C	ΔH_r kcal/mol Exp.	ΔH_r kcal/mol Calc.[c]	ΔS_r cal/mol deg Exp.	ΔS_r cal/mol deg Calc.[c]
1) $2\ CF_3CCl{=}CFCl \rightleftharpoons CF_3CCl{=}CF_2 + CF_3CCl{=}CCl_2$	350-450	-2.50 ± 0.38	-2.1	-3.61 ± 0.57	0.4
2) $\underline{\text{cis}}\text{-}CF_3CCl{=}CFCl \rightleftharpoons \underline{\text{trans}}\text{-}CF_3CCl{=}CFCl$	350-450	-0.30 ± 0.08	0	0.24 ± 0.21	0
3) $2\ CF_3CF{=}CFCl \rightleftharpoons CF_3CF{=}CF_2 + CF_3CF{=}CCl_2$	200-300	-2.65 ± 0.14	-2.1	-2.69 ± 0.28	0.3
4) $\underline{\text{cis}}\text{-}CF_3CF{=}CFCl \rightleftharpoons \underline{\text{trans}}\text{-}CF_3CF{=}CFCl$	200-300	-0.56 ± 0.10	0	0.24 ± 0.20	0
5) $CF_3CF{=}CFCl + CF_3CCl{=}CFCl \rightleftharpoons CF_3CF{=}CF_2 + CF_3CCl{=}CCl_2$[b]	300	-1.38 ± 0.15	-2.1	-2.92 ± 0.24	0.3

[a] Heats of reaction (ΔH_r) were determined from slopes of plots of $\log_{10}K_p$ *vs*. $1/T$.

Entropies of reaction (ΔS_r) were derived from the equation $\Delta S_r = (\Delta H_r/T) + 2.3026\ R\log_{10}K_p$.

Values used in these calculations were taken from Tables 2, 3 and 4.

Error ranges equal $\pm$ two standard errors.

[b] Thermochemical property values derived from those of eqn. (1), (2) and (3) in the text.

[c] Calculated according to method of Benson, *et al*. [3].

TABLE 2

Equilibrium Composition of
2 $CF_3CF{=}CFCl \rightleftharpoons CF_3CF{=}CF_2 + CF_3CF{=}CCl_2$[a]

T, °C	C/T, sec	Equilibrium Partial Pressures, atm x 10^1			
		t-$CF_3CF{=}CFCl$	c-$CF_3CF{=}CFCl$	$CF_3CF{=}CF_2$	$CF_3CF{=}CCl_2$
201	5	0.67	0.33	2.02	2.07
201	9	0.63	0.30	1.89	1.95
251	5	0.68	0.35	1.90	1.89
251	9	0.71	0.37	1.96	2.00
300	5	0.77	0.42	1.90	1.94
300	9	0.73	0.39	1.77	1.81

[a] Catalyst = Cr_2O_3

[b] Total pressure = 1.009 atm (C/T = 9 sec); 1.005 (C/T = 5 sec) Inert gas = nitrogen

TABLE 3

Equilibrium Composition of
2 $CF_3CCl{=}CFCl \rightleftharpoons CF_3CCl{=}CF_2 + CF_3CCl{=}CCl_2$[a]

T, °C	C/T, sec	Equilibrium Partial Pressures, atm x 10^1			
		t-$CF_3CCl{=}CFCl$	c-$CF_3CCl{=}CFCl$	$CF_3CCl{=}CF_2$	$CF_3CCl{=}CCl_2$
449	4	1.12	0.81	1.62	1.94
450	8	1.06	0.76	1.50	1.86
400	4	1.06	0.76	1.58	1.95
399	8	1.03	0.73	1.52	1.96
349	4	0.99	0.69	1.57	2.07
350	8	0.99	0.69	1.54	1.99

[a] Catalyst = Cr_2O_3

[b] Total pressure = 1.008 (C/T = 8 sec), 1.018 (C/T = 4 sec.); Iner gas = Nitrogen. A byproduct, $CF_3CHClCF_3$ (partial pressures of 0.01-0.03 atm) was formed over the temperature range studied.

TABLE 4

Equilibrium Composition of 2 $CF_3CF{=}CF_2$ + 2 $CF_3CCl{=}CCl_2$ $\rightleftharpoons$ $CF_3CF{=}CFCl$ + $CF_3CF{=}CCl_2$ + $CF_3CCl{=}CFCl$ + $CF_3CCl{=}CF_2$[a]

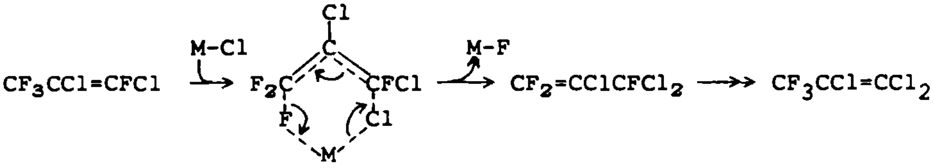
		Equilibrium Partial Pressures, atm x 10							
T, °C	C/T, sec	$CF_3CF{=}CF_2$	$CF_3CCl{=}CCl_2$	c-$CF_3CF{=}CFCl$	t-$CF_3CF{=}CFCl$	$CF_3CF{=}CCl_2$	c-$CF_3CCl{=}CFCl$	t-$CF_3CCl{=}CFCl$	$CF_3CCl{=}CF_2$
226	2.7	0.77	0.51	0.21	0.42	1.99	0.25	0.37	1.78
226	5.3	0.71	0.40	0.19	0.38	1.70	0.20	0.31	1.52
251	2.7	0.80	0.51	0.24	0.44	1.92	0.26	0.39	1.69
251	5.3	0.67	0.44	0.21	0.41	1.66	0.22	0.33	1.45
275	2.7	0.72	0.59	0.23	0.45	1.87	0.29	0.43	1.66
275	5.3	0.63	0.49	0.21	0.39	1.56	0.25	0.36	1.42
301	2.7	0.83	0.50	0.28	0.53	1.34	0.28	0.41	1.53
303	5.4	0.75	0.39	0.23	0.43	1.70	0.24	0.34	1.40
350	1.7	0.53	0.93	0.25	0.46	1.75	0.41	0.59	1.46
349	2.7	0.63	0.70	0.25	0.45	1.50	0.36	0.52	1.56

[a] Catalyst = Cr_2O_3

[b] Total pressures = 1.08 atm (C/T = 5.4 sec); 1.21 atm (C/T = 2.7 sec); 1.30 atm (C/T = 1.7 sec).
Inert gas = nitrogen. A byproduct, $CF_3CFClCF_3$ (partial pressures of 0.01-0.03 atm) was observed at 300-350°C.

Verification that equilibrium had been reached in these reactions was complicated by the formation of byproducts. For all reactions the contact times were varied at each temperature in attempting to verify that equilibrium had been achieved. However, due to side reactions, the reactions often appeared to proceed slightly further at the longer contact times. For reactions (1) and (2), final verification that equilibria had indeed been achieved was obtained by carrying out the reverse reactions (The equilibrium compositions reported for reaction (2) in Table 1 are taken from the reverse reaction). In both cases, the product compositions were identical to those obtained from the forward reactions, within experimental error. Since reaction (3) involves similar exchange processes, it was presumed from the similar variations with contact time that equilibrium had been reached. Finally, plots of the calculated $\log_{10}K_p$ vs. 1/T for all of these reactions were linear, as expected for the equilibrium state.

The presence of allylic halogens in these compounds makes it likely that such halogens are participating in the exchange reactions. However, compounds containing chlorine substituents on the sp^3 terminal carbons were not found among the products of these reactions. We believe that such compounds are likely intermediates in these exchange reactions but rapidly isomerize, through similar exchange mechanisms, to the more stable CF_3-containing isomers, e.g.,



The preferred stability of the CF_3-containing products over the others was independently verified through calculations of the free energies of formation of these compounds using a group additivity method reported by Benson, et al. [3].

The thermochemical properties measured in this study enabled a test of the group additivity procedure [3] for the determination of the thermochemical properties of organic compounds. Using this procedure and recently updated group property values for fluorocarbons [4], we calculated the relevant thermochemical property values for equilibria (1), (2) and (4) (cf. Table 1). As seen from Table 1, the calculated heats of reaction are in excellent agreement with those found experimentally. This finding is at least partially fortuitous since this calculational method does not usually produce such close agreement with experiment, especially for fluorocarbons. The agreement of the calculated entropies of reaction with the experimental values is less close but is still within the expected error of the calculational method. Overall, these results show that the additivity of thermochemical properties associated with the groups $=CCl_2$, $=CF_2$ and $=CFCl$ in chlorofluoropropylenes is a valid procedure, within the calculational error originally reported.

Chlorofluoroethylenes

Attempts to measure the thermochemical properties of exchange reactions of chlorofluoroethylenes using either AlF_3 or Cr_2O_3 as catalysts were not successful due to the formation of byproducts that obscured the equilibria. The reactions were also observed to be less facile than those involving the chlorofluoropropylenes. We initially examined the disproportionation of 1-chloro-1,2,2-trifluoroethylene over Cr_2O_3 at temperatures ranging from 200 to 350°C:

$$CFCl{=}CF_2 \longrightarrow CF_2{=}CF_2 + CF_2{=}CCl_2 + CFCl{=}CFCl \qquad (8)$$

The disproportionation proceeded to conversions as high as 81% at contact times up to 7 seconds. However, considerable variation in conversions were noted with changes in contact time. In addition, the formation of byproducts, mainly CF_3CF_2Cl and $CF_3CF{=}CFCF_3$, increased significantly with increases in temperature and contact time.

The reverse of reaction (8) was also examined but, while $CFCl{=}CF_2$ was the major product, equilibrium again could not be verified due to extensive byproduct formation.

The formation of both $CF_2{=}CCl_2$ and $CFCl{=}CFCl$ in this disproportionation appears to be a direct result of the reaction since these compounds do not appear to be easily interconverted when reacted separately over Cr_2O_3. Instead, individual disproportionations occur:

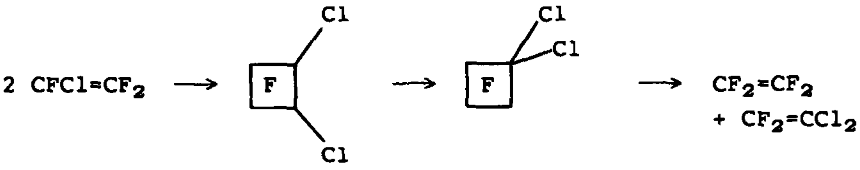
$$2\ CF_2{=}CCl_2 \xrightarrow{275\text{-}326^\circ C} CF_2{=}CFCl + CFCl{=}CCl_2 \qquad (9)$$

$$2\ CFCl{=}CFCl \xrightarrow{275\text{-}375^\circ C} CF_2{=}CFCl + CFCl{=}CCl_2 \qquad (10)$$

Since allylic halogens are not present in these compounds, the mechanism(s) by which these disproportionations proceed remains obscure. A brief study of reaction (8) was made to obtain additional information regarding the probable reaction pathways. A possible mechanism was suggested by the formation of trace quantities of CF_3CF_2H during these reactions. A sequential addition/elimination of adventitious hydrogen halides was considered as a possible pathway:

$$CFCl{=}CF_2 \xrightarrow{HCl} CFCl_2CHF_2 \xrightarrow{-HF} CCl_2{=}CF_2$$

However, addition of small amounts of either HCl or HF to these reactions actually supressed the disproportionations. Another possible mechanism involving the intermediacy of the thermal dimer of $CFCl{=}CF_2$, 1,2-dichlorohexafluorocyclobutane, was also discounted by demonstrating the lack of reactivity of this compound under typical reaction conditions:



Finally, the intermediacy of saturated perhalogenated ethanes, arising from side reactions, in these disproportionations is not likely. These materials could serve as intermediates in pathways involving the halogenation/dehalogenation of the fluoroolefins. However, addition of small amounts of CF_2ClCF_2Cl, for example, to these reactions caused no significant rate changes. Further work is needed, however, to establish the importance of this pathway.

A likely mechanism involves the direct halogen exchange of the chlorofluoroethylenes with halogenated metal oxide sites. In support of this, the disproportionations often exhibited induction periods indicating a need for the initial formation of halogenated metal species.

EXPERIMENTAL

All reactions were carried out by passing the reactant gases through a 1/4" x 3" 304 stainless steel tubular reactor containing the appropriate catalyst. The reactor temperature was controlled by immersion of the reactor in a fluidized silicon carbide bath maintained at constant temperature. All gases were delivered to the reactor by calibrated Tylan mass flow controllers. Liquids were fed to the reactor by first vaporizing the liquid by passing through a heated silicon carbide bed. All contact times are defined as: C/T = (bed volume of catalyst)/(total gas flowrate, referenced to 0°C and 1 atm pressure). Product gases were analyzed using a Hewlett Packard 5400 Gas Chromatograph. A 15' x 1/8" Krytox on 60/80 Carbopak BHT column was used in the analysis. All compounds were identified by comparison with authentic samples or, when not available, by ^{19}F NMR of isolated material. Effluent gases were scrubbed in 30% aqueous KOH.

The compounds $CF_2{=}CCl_2$, $CFCl{=}CFCl$, $CF_3CCl{=}CF_2$, $CF_3CCl{=}CF_2$ were obtained from PCR Incorporated. The compounds $CF_2{=}CFCl$ and $CF_3CF{=}CF_2$ were obtained from Matheson Gas Products, Inc. The compounds $CF_3CF{=}CCl_2$ and $CF_3CF{=}CFCl$ were synthesized by reacting $CF_3CF{=}CF_2$ with $AlCl_3$ [5]. The Cr_2O_3 used (S.A. = 42.4 m^2/g; particle size = 25-30 mesh) was prepared by the pyrolysis of anhydrous ammonium dichromate. The $AlF_3.3H_2O$ used was purchased from Johnson Matthey, Inc.

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