

A KINETIC STUDY ON THERMAL CHLORINATION OF 1-CHLORO-2,2,2-TRIFLUOROETHANE

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Abstract—HCFC-133a (1-chloro-2,2,2-trifluoroethane) was thermally chlorinated in an integral reactor under atmospheric pressure in a temperature range between 573 and 723 K. From the analysis of the data it was confirmed that the reaction was a two-step series-parallel reaction and each step was a second-order reaction. The ratio of the second-step rate constant to the first-step rate constant did not change with temperature and its value was 1.13. The activation energy was 106 kJ/g-mol. These results indicate that the product distribution is the sole function of conversion of HCFC-133a.

INTRODUCTION

Recognition of the adverse effect of fully halogenated chlorofluorocarbons (CFCs) on stratospheric ozone levels has led to an international effort to eliminate the use and production of CFCs. Industry and research institutions are actively developing and testing a variety of options for the phase-out of CFCs, and the best option at present stage is regarded to be replacement of CFCs with environmentally acceptable alternatives such as hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) [1, 2]. Among them HCFC-123 (1,1-dichloro-2,2,2-trifluoroethane) has low ozone depletion potential (ODP=0.021) and is promised as one of alternatives to replace CFC-11 (CCl₃F) which is widely used as a blowing agent and a refrigerant [3].

HCFC-123 can be manufactured by a variety of processes [4-8], and one of the production methods is thermal (homogeneous) chlorination of HCFC-133a (1-chloro-2,2,2-trifluoroethane) with chlorine under atmospheric pressure [9, 10] or under high pressure [11]. The thermal chlorination of HCFC-133a is considered a two-step series-parallel reaction, since it has been observed that HCFC-133a is first chlorinated to HCFC-123, the desired product, and it is further chlorinated to CFC-113a (1,1,1-trichloro-2,2,2-trifluoroethane). This information should be taken into account in the production of HCFC-123, and in order to estimate the product distribution one of the basic data needed is the kinetic information. However, the kinet-

ics for the chlorination has rarely been reported and discussed fully yet. In this work the thermal chlorination of HCFC-133a was carried out in an integral reactor under atmospheric pressure in a temperature range between 573 and 723 K and the rate equations were proposed. Some factors affecting the product distribution were also discussed.

RATE EQUATIONS

Suppose the chlorination of HCFC-133a proceeds as follows:



where A=HCFC-133a, B=Cl₂, R=HCFC-123, S=CFC-113a, and k₁ and k₂ are rate constants. Reactions (1) and (2) represent a typical series-parallel reaction. In many cases thermal chlorination of hydrocarbons is reported to be a second-order reaction [12-15], and thus it is not unreasonable to assume that the reaction order is the same for the chlorination of HCFC-133a. The analysis procedure for the kinetics of this type of reaction is well known [15]. The formation rates of the compounds are as follows:

$$r_A = \frac{dC_A}{dt} = -k_1 C_A C_B \quad (3)$$

$$r_B = \frac{dC_B}{dt} = -k_1 C_A C_B - k_2 C_R C_B \quad (4)$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A C_B - k_2 C_R C_B \quad (5)$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R C_B \quad (6)$$

Dividing Eq. (5) by Eq. (3) we obtain:

$$\frac{dC_R}{dC_A} = \alpha \frac{C_R}{C_A} - 1 \quad (7)$$

where $\alpha = k_2/k_1$. When $C_A = C_{A0}$ and $C_R = 0$ at the tubular reactor inlet, the solution is:

$$\frac{C_R}{C_{A0}} = (1 - X_A) \ln \frac{1}{1 - X_A} \quad \text{for } \alpha = 1 \quad (8)$$

$$\frac{C_R}{C_{A0}} = \frac{1}{1 - \alpha} [(1 - X_A)^\alpha - (1 - X_A)] \quad \text{for } \alpha \neq 1 \quad (9)$$

where X_A = conversion of A. If the selectivity of R, S_R , is defined as (moles of R formed)/(moles of A consumed), it is expressed as:

$$S_R = \frac{1}{X_A(1 - \alpha)} [(1 - X_A)^\alpha - (1 - X_A)] \quad \text{for } \alpha \neq 1 \quad (10)$$

The value of α can be determined by analyzing the experimental data using Eq. (8), (9) or (10).

The rate constant k_1 can be determined as follows. The performance equation for the integral tubular reactor is:

$$\frac{V}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A} = \int_0^{X_A} \frac{dX_A}{k_1 C_{A0} (1 - X_A) C_B} \quad (11)$$

Dividing Eq. (4) by Eq. (3) gives:

$$\frac{dC_B}{dC_A} = 1 + \alpha \frac{C_R}{C_{A0}(1 - X_A)} \quad (12)$$

Using that $C_A/C_{A0} = 1 - X_A$ and introducing Eq. (9) into Eq. (12), we obtain:

$$-\frac{1}{C_{A0}} \frac{dC_B}{dX_A} = 1 + \frac{\alpha}{\alpha - 1} - \frac{\alpha}{\alpha - 1} (1 - X_A)^{\alpha-1} \quad (13)$$

The solution of Eq. (13) is:

$$C_B = C_{A0} \left\{ \frac{C_{B0}}{C_{A0}} - (1 + X_A) + \frac{1}{\alpha - 1} \right. \\ \left. [\alpha(1 - X_A) - (1 - X_A)^\alpha] \right\} \quad (14)$$

Introducing Eq. (14) into Eq. (11) gives:

$$\frac{V}{F_{A0}} = \frac{1}{k_1 C_{A0}^2} F(X_A) \quad (15)$$

where

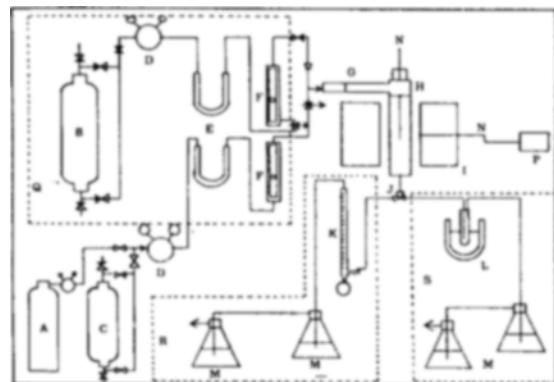


Fig. 1. Schematic diagram of the reaction apparatus.

A: N ₂ cyclinder	J: Three-way cock
B: HCFC-133a storage vessel	K: Soap-bubble flowmeter
C: Cl ₂ storage vessel	L: Dry ice-acetone trap
D: Pressure regulator	M: Aqueous NaOH absorber
E: CaCl ₂ trap	N: Thermocouple
F: Rotameter	P: Temperature controller
G: Preheating tube	Q: Acryl box
H: Reactor	R: Venting section
I: Heater	S: Sampling section

$$F(X_A) = \frac{\int_0^{X_A} \frac{dX_A}{(1 - X_A) \left\{ \frac{C_{B0}}{C_{A0}} - (1 + X_A) + \frac{1}{\alpha - 1} [\alpha(1 - X_A) - (1 - X_A)^\alpha] \right\}}}{dX_A} \quad (16)$$

Eq. (15) can be rewritten as follows:

$$F(X_A) = k_1 C_{A0} \tau \quad (17)$$

where $\tau = V/v$ = space time. The volumetric flow rate of the feed v may be defined at ambient conditions, and so may be C_{A0} and the space time. The value of k_1 can thus be determined from the slope of the line which is constructed by plotting $F(X_A)$ versus $C_{A0} \tau$.

EXPERIMENTAL

1. Chemicals

HCFC-133a was supplied from Onda Chemicals (Japan), and Cl₂ was supplied from Baek Kwang Chemicals. Reagent-grade granular anhydrous CaCl₂ was used for the moisture traps and reagent-grade NaOH was used for the absorbers. The reactor tube was filled with silica gel beads which had 2-3 mm of diameter and ca. 500 m²/g of surface area. The silica gel

beads were inert for the reaction and were used in order to get even flow distribution and better heat transfer in reactor.

2. Reaction experiments

The schematic diagram of the reaction apparatus is shown in Fig. 1. The storage cylinder for liquid HCFC-133a was placed in an acryl box, and the temperature in the box was maintained at around 320 K in order to obtain high enough pressure to feed the HCFC-133a which was vaporized in the attached vertical tube. Each of HCFC-133a and Cl_2 vapors passed through a pressure regulator, a CaCl_2 moisture trap and a rotameter. The pressure regulator for Cl_2 vapor was made of stainless steel. The vapors were mixed, passed through a preheating tube which was maintained at around 473 K and flowed into the reactor. The reactor was a 1/2 in. \times 0.4 m Monel tube. The reaction temperature was controlled by an electric heater, and the effective reaction zone was 12 cm long and 3.39 cm³ in volume. Most of tubes and fittings in which Cl_2 and HCl flowed were made of teflon or glass. A N_2 flow line was attached as shown in Fig. 1 in order to flush the system when necessary.

The effluent from the reactor flowed out through the venting section during the initial unsteady state or through the sampling section during the sampling which was made by liquefying the reaction mixture in a dry ice-acetone trap. After an appropriate amount of the liquid was collected in the sampling tube, the bath was removed, and the liquid in the sampling tube was mixed with 15 wt% aqueous NaOH solution which was pre-chilled to 253 K to remove all the residual Cl_2 and trace of HCl. The liquid mixture was settled down to separate into two layers.

The organic liquid was analyzed by a GC. The column used was a 1/8 in. \times 3 m Porapak Q 80/100 mesh column; the oven temperature was 473 K; the carrier gas was 20 cm³/min of He. The detector used was TCD and the relative molar response values for HCFC-133a, HCFC-123 and CFC-113a, which were determined from a standard mixture, were 87, 122 and 135 (benzene=100), respectively.

RESULTS AND DISCUSSION

1. Determination of α value

The reaction results are shown in Table 1. The conversion of A was decreased with increasing feed rate and A/B ratio as expected.

C_R/C_{A0} and S_R were plotted against X_A as shown in Figs. 2 and 3. The data points obtained at the same temperature, especially at 643 K, appeared to fall on

Table 1. Results for the thermal chlorination of HCFC-133a

Run no.	Reaction temp. [K]	Flow rate (cm ³ /min at 298 K & 1 atm)		Composition of effluent* (mole%)			S_R
		A	B	A	R	S	
1	573	30	30	94.1	5.4	0.5	0.915
2		50	50	96.5	3.2	0.3	0.914
3	623	30	30	71.9	22.9	5.2	0.815
4		50	50	81.8	16.0	2.2	0.879
5	643	30	30	53.2	30.5	16.1	0.655
6		50	50	64.5	28.2	7.2	0.797
7		60	60	72.1	22.4	5.5	0.803
8		70	70	76.7	19.3	4.0	0.828
9		80	80	79.7	17.3	3.0	0.852
10		100	100	82.2	15.0	2.8	0.843
11		60	40	69.7	24.8	5.5	0.828
12		40	60	61.8	28.8	9.4	0.854
13		70	30	80.6	17.6	1.8	0.907
14	673	30	30	38.2	35.1	26.3	0.572
15		50	50	50.4	31.5	18.1	0.635
16		60	60	51.8	32.7	15.5	0.678
17		80	80	54.0	32.1	13.9	0.698
18		100	100	64.3	25.2	10.4	0.708
19	703	30	30	33.0	34.2	32.8	0.510
20		50	50	37.0	34.7	28.3	0.551
21		60	60	43.0	33.5	23.5	0.588
22		80	80	44.2	33.0	22.8	0.591
23		100	100	48.8	34.0	17.2	0.664
24	723	30	30	31.0	34.3	34.7	0.497
25		50	50	35.0	37.8	27.2	0.582
26		80	80	36.8	34.6	28.6	0.547

* Cl_2 and HCl are excluded.

a smooth curve. This indicates that the assumption that both Reactions (1) and (2) are second order can be justified since Eq. (9) or Eq. (10) suggests that as long as α is constant C_R/C_{A0} or S_R is a function of X_A only and is independent of $\text{C}_{B0}/\text{C}_{A0}$. In other words, it can be said that the chlorination of HCFC-133a proceeds via a two-step series-parallel reaction and each step is an irreversible second-order reaction, being first order with respect to each of Cl_2 and the HCFC.

An interesting feature was noted in Figs. 2 and 3. That is, all the data points appeared to fall on a single line regardless of the reaction temperature. This means that α is independent of temperature; in other words the activation energies for Reactions (1) and (2) are practically the same. Reactions of hydrocarbons with chlorine are well known to follow the substitution chlorination (chain reaction) mechanism [16]. The

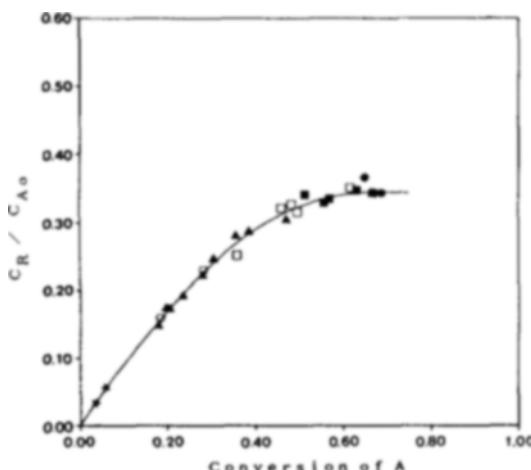


Fig. 2. Fractional yield of HCFC-123 vs. conversion of HCFC-133a for thermal chlorination.

★: 573 K, ○: 623 K, ▲: 643 K, □: 673 K, ■: 703 K, ●: 723 K.

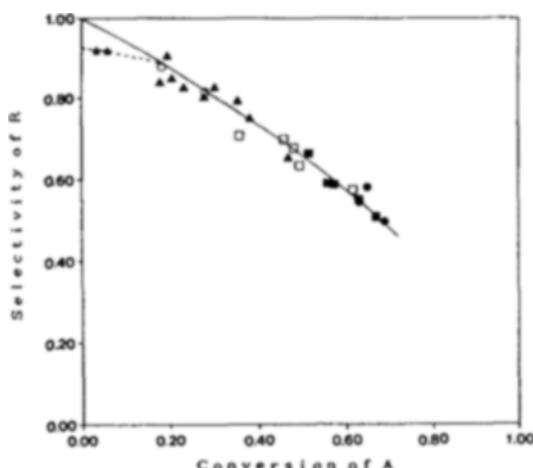
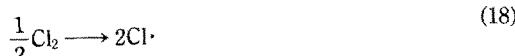


Fig. 3. Selectivity of HCFC-123 vs. conversion of HCFC-133a for thermal chlorination.

★: 573 K, ○: 623 K, ▲: 643 K, □: 673 K, ■: 703 K, ●: 723 K.

reaction of HCFC-133a with chlorine may be expected to follow the mechanism analogous to it, as shown below:

Initiation



Propagation

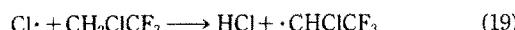


Table 2. Comparison of S_R data in the literature with calculated S_R

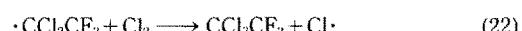
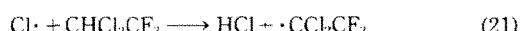
Temp. [K]	Pressure	$\frac{C_{B_0}}{C_{A_0}}$	X_A	S_R	Calculated $S_R^{(1)}$
(a) Data in Ref. 10					
673	1 atm	1/9	0.10	0.91	0.941
673	1 atm	1/4	0.22	0.86	0.867
673	1 atm	3/7	0.40	0.77	0.741
(b) Data in Ref. 11 ⁽²⁾					
523	120 bar	0.27	0.244	0.833	0.851
523	127 bar	0.51	0.409	0.722	0.735
523	122 bar	0.58	0.451	0.679	0.702
473 ⁽³⁾	62 bar	0.26	0.237	0.859	0.856
493 ⁽³⁾	70 bar	0.58	0.218	0.867	0.868
453 ⁽⁴⁾	50 bar	0.26	0.230	0.856	0.860
453 ⁽⁴⁾	55 bar	0.58	0.388	0.744	0.750

1) Calculated from Eq. (10) with α value of 1.13.

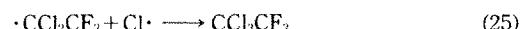
2) Reactions were carried out under supercritical conditions. Conversions of B were over 0.99.

3) CCl_4 was added.

4) A free-radical initiator was used.



Termination



Steps (19)-(22) are very fast reactions and their activation energies are near zero; therefore the overall activation energies for Reactions (1) and (2) are, in theory regardless of the HCFC species, equal to the activation energy for Step (18) [16].

Over the temperature range studied the value of α which gave the best fit of the data was determined to be 1.13. The solid lines in Figs. 2 and 3 denote the product distribution is determined solely by X_A , but not directly influenced by temperature and C_{B_0}/C_{A_0} . It is generally known for alkanes that a hydrogen atom on a more substituted carbon is more readily replaced by another halogen atom [9, 16]. The α value obtained in this work conforms to this expectation. However, the difference between k_1 and k_3 is not substantial.

The selectivity of R reported in Refs. 10 and 11 was compared with that in this work which was obtain-

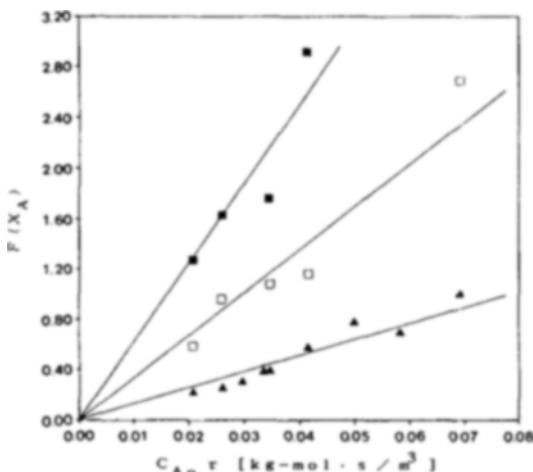


Fig. 4. Plot of $F(X_A)$ vs. $C_{A_0}\tau$ for thermal chlorination of HCFC-133a.

▲: 643 K, □: 673 K, ■: 703 K.

Table 3. Values of the rate constant k_1

Reaction temp.[K]	573	623	643	673	703	723
$k_1 [m^3/kg \cdot mol \cdot s]$	0.952	5.22	12.1	33.8	61.8	97.2

ed from Eq. (10). As shown in Table 2, the selectivities agree very well with each other. This strongly supports independence of α from temperature and general applicability of Eq. (10), at least under atmospheric pressure, and this also suggests that application of Eq. (10) can be extended over wider ranges of reaction conditions.

According to Eq. (10), S_k should approach to 1 as X_A approaches to 0. However, as shown by the dotted line in Fig. 3 S_k values at low conversions were somewhat smaller than the calculated values. This is probably due to a longer residence time of a portion of the reacting gas which has entered stagnant regions in the porous silica gel. When the reaction temperature was higher and hence the conversion was high enough, the effect of stagnant regions would not be as significant as in the above case.

2. Rate constant k_1

Plots of $F(X_A)$ versus $C_{A_0}\tau$ for three temperatures were shown in Fig. 4. Fairly good straight lines could be drawn, and the k_1 values were determined from the slopes. The k_1 values are shown in Table 3. The numbers of data at 573 and 623 K were too a few to draw lines, but as the k_1 values calculated from Eq. (17) were very close to each other average values were taken.

Chlorine balance was set up by assuming that chlo-

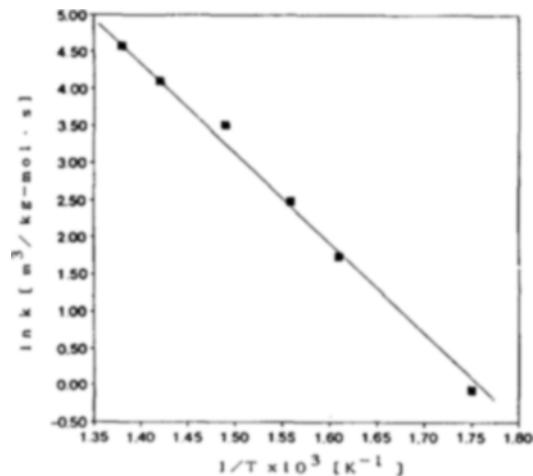


Fig. 5. Arrhenius plot for k_1 .

rine was consumed exactly by Reactions (1) and (2), and the chlorine consumed in Run No. 24 turned out to exceed the chlorine fed; the conversion of chlorine for Run No. 19 was very close to 1. This suggests that chlorination occurred partly by the reaction of HCFCs with HCl, probably at high temperatures and at high conversions of B. In fact, it has been reported that while hydrochlorination of alkanes and alkyl chlorides occurs slowly in the absence of a catalyst it can be catalyzed by a small amount of chlorine [16]. The k_1 values calculated from Eq. (17) for Run Nos. 19 and 24 were unreasonably high, and thus they were not used in evaluating the k_1 values. The k_1 value at 723 K was also evaluated by averaging the two values from Run Nos. 25 and 26.

The rate constants k_1 were plotted against $1/T$ (Fig. 5), and the obtained result was:

$$k_1 = 4.70 \times 10^9 \exp(-E/RT) \quad [m^3/kg \cdot mol \cdot s] \quad (26)$$

where the activation energy E was 106 kJ/g-mol. This value is comparable to the theoretical activation energy for Step (18), 119 kJ/g-mol, which was calculated by the bond-energy method [16].

CONCLUSIONS

For the thermal chlorination of HCFC-133a with chlorine the following results are obtained;

1. The chlorination proceeds via a two-step series-parallel reaction and each step is an irreversible second-order reaction.

2. The ratio of the rate constants α ($= k_2/k_1$) is 1.13, and it is independent of temperature.

3. The rate constant k_1 is:

$$k_1 = 4.70 \times 10^9 \exp(-E/RT) \quad [\text{m}^3/\text{kg}\cdot\text{mol}\cdot\text{s}]$$

where $E = 106 \text{ kJ/g-mol}$.

ACKNOWLEDGEMENT

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NOMENCLATURE

A	: HCFC-133a
B	: Cl_2
C_i	: concentration of component i ($i = A, B, R$ or S)
C_{in}	: concentration of component i at reactor inlet [kg-mol/m ³]
E	: activation energy [kJ/g-mol]
F_{A0}	: molar feed rate of A [kg-mol/s]
$F(X_A)$: function of X_A defined by Eq. (16)
k_1, k_2	: rate constants [m ³ /kg-mol·s]
R	: HCFC-123, or gas law constant
r_i	: reaction rate for compound i [kg-mol/m ³ ·s]
S	: CFC-113a
S_R	: selectivity of R
t	: time [s]
V	: volume of reactor [m ³]
v	: volumetric feed rate [m ³ /s]
X_A	: conversion of A [-]
α	: k_2/k_1 [-]
τ	: space time ($= V/v$) [s]

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