Pyrolysis of 1,1-Dichloro-1-Fluoroethane in the Absence and Presence of Added Propene or CCl₄: A Computer-Aided Kinetic Study

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ABSTRACT: The thermal dehydrochlorination $CCl_2FCH_3 \rightarrow CCIF = CH_2 + HCl$ has been studied in a static system between 610 and 700 K at pressures ranging from 14 to 120 torr. The experiments were performed in the absence and presence of an added inhibitor (0.5 to 7 torr of C_3H_6) or catalyst (2 to 8 torr of CCl_4). The evolution of the reaction was followed by measuring the pressure rise in the quartz reaction vessel and analyzing the products by gas chromatography. All the experimental results can be explained quantitatively in terms of a reaction model both radical and molecular. The molecular dehydrochlorination has an activation energy of 57.05 kcal/mol and a preexponential factor of $10^{14.02}$ s⁻¹. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 33: 191–197, 2001

INTRODUCTION

Kinetic and mechanistic studies in our laboratory have shown that the thermal dehydrochlorination of CCl_3CH_3 is mainly a radical reaction [1], while that of $CClF_2CH_3$ is molecular [2,3]. This work deals with the intermediate case of CCl_2FCH_3 (Freon 141b), which completes the series $CCl_{3-n}F_nCH_3$, with n = 0-2.

Sianesi et al. [4] studied the elimination of HCl from CCl_2FCH_3 in a Pt tubular reactor between 803 and 853 K at pressures ranging from 100 to 760 torr. These authors observed first-order kinetics with an activation energy of only 47 kcal/mol. They attributed this low value to a predominant radical pathway, al-

though the inhibitory effect of added NO they measured was weak.

It seemed, therefore, interesting to us to reinvestigate the reaction in the same conditions as those previously used in the cases of CCl_3CH_3 [1] and $CClF_2CH_3$ [2,5]. The experiments were thus performed in the same conditioned quartz static reaction vessel in the absence and presence of added C_3H_6 or CCl_4 .

EXPERIMENTAL

 CCl_2FCH_3 (Solvay), propene (Messer-Griesheim), and CCl_4 (UCB), 99.95, 99.98, and 99.997% pure, respectively, were used without further purification.

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The pyrolysis of CCl₂FCH₃ was followed by measuring the variation of the total pressure with a Pyrex Bourdon gauge. The conventional static system, the cylindrical quartz reaction cell (surface-to-volume ratio *S/V* of about 1.2 cm⁻¹, V = 100 mL), and the technique were the same as in the previous studies of the pyrolyses of CCl₃CH₃ [1] and CClF₂CH₃ [2,5]. The reactor walls were conditioned by pyrolyzing several times large amounts of CCl₂FCH₃ at high temperature (723 K). The GC-analyses of the reaction products were performed on a 2-m column of 25% w/w Silicone OV101 on 60–80 mesh Chromosorb PAW at 60°C.

More than 100 experiments were carried out. The analyses showed that, in the absence and presence of added propene or CCl_4 , 1-chloro-1-fluoroethene and 1,1-dichloroethene are formed according to the parallel reactions

$$CCl_2FCH_3 \longrightarrow CClF = CH_2 + HCl$$
 (1)

and

$$CCl_2FCH_3 \longrightarrow CCl_2 = CH_2 + HF$$
 (2)

No other products are detected. The dehydrochlorination (1) yields reproducible results but not the dehydrofluorination (2). The latter reaction, which is about 10 times slower than the former (100 times when CCl_4 is added), is most probably heterogeneous (see later) and has not been studied. The $CCIF=CH_2$ concentration-time profile of the dehydrochlorination was obtained from the pressure rise in the reaction vessel corrected for the small contribution of the dehydrofluorination. It also appears from the analyses that the added C_3H_6 and CCl_4 are hardly consumed in the course of the reaction.

NUMERICAL MODELING OF THE EXPERIMENTAL RESULTS

The numerical modeling procedure is similar to that given in [1,5-7]. The molecular and radical reaction model used is based on that for the pyrolyses of CCl_3CH_3 [1] and $CClF_2CH_3$ [5]. The Arrhenius parameters, *E* and *A*, are either known or estimated; this also holds for the thermochemical parameters used to calculate *E* and *A* for back reactions from the "principle of microscopic reversibility." Using OPTKIN [8], this reaction model could be reduced, by repeated simulations and optimizations, to the reaction steps and the parameters given in Tables I and II. The steps are the molecular reactions (1) and (-1), the radical chain

initiation (2),¹ the chain propagations (3) and (4) and their reverses, the radical transfer reactions (5) and (6) and their back reactions, and the chain terminations (-2), (7), and (8), the last one being heterogeneous.

When CCl_4 is added, the chain initiation (2) is replaced by the faster step (9) followed by the transfer steps (10) to (12) and their reverses, and the chain terminations become the radical recombinations (-9), (13), and (14).

Steps (-1), (-3), (-11), and (-13) are minor reactions for all experimental conditions used in this work.

The reduction procedure involved a set of seven typical experiments (three in the absence and four in the presence of added C_3H_6 or CCl_4), with reaction conversions going up to about 20%. All their points are shown in the figures given later, together with the $CClF=CH_2$ concentration-time profiles optimized by means of OPTKIN. The corrections that were applied to the initial values of the kinetic and thermodynamic parameters to obtain these profiles are given in Tables I and II, respectively. As can be seen, their values are small. They are less than 0.6 kcal/mol for activation energies and 0.2 log units for A-factors. The maximum corrections on heats of formation and entropies amount to -0.6 kcal/mol and 0.89 cal/mol K, respectively.

RESULTS AND DISCUSSION

Pyrolysis of CCl₂FCH₃

The dehydrochlorination of CCl_2FCH_3 has been studied between 650 and 700 K. The pressure ranged from 14 to 120 torr. Figures 1 and 2 show typical CClF = CH_2 concentration-time profiles for different temperatures and pressures. As can be seen, the reaction observed, which is only slightly faster than the molecular reaction at the beginning, accelerates markedly with time and is well described by the optimized model given in Table I. Note that the initial model already yields reasonable results (see Fig. 1).

Analyses of the rates of the elementary reaction steps show that the autoacceleration actually results mainly from the radical step (6). This reaction converts the unreactive \cdot CClFCH₃ radicals (formed in the initiation step (2) and in the transfer step (5)) into Cl chain carriers due to the HCl produced by the molec-

¹The C—Cl BDE in $CFCl_2CH_3$ calculated from Table II is 79 kcal/mol. This value is much lower than values for other BDEs in this molecule obtained from Table II, [1], [14], and [20]: These values are 93, 103, and 113 kcal/mol for the C—C, C—H, and C—F bonds, respectively. Reaction (2) is therefore likely the primary initiation step for radical formation.

| | E | | | $\log_{10}A$ | | |
|--|---|-----------------------|-------|---|-----------------------|-------|
| | Initial | Optim. | Corr. | Initial | Optim. | Corr. |
| a. Molecular reaction $CCl_2FCH_3 \xrightarrow[-1]{-1} CClF = CH_2 + HCl$ | 57.00 ^b 37.50 ^c | 57.05 38.17 | 0.05 | 14.00 ^b 7.74 ^c | $\frac{14.02}{7.94}$ | 0.02 |
| b. Radical reactions $CCl_2FCH_3 \stackrel{2}{\longleftarrow} \cdot CClFCH_3 + Cl$ | $\frac{77.53^{\circ}}{0.00^{d}}$ | $\frac{76.52}{0.00}$ | | 15.84° 10.30 ^d | $\frac{16.00}{10.35}$ | 0.05 |
| $Cl + CCl_2FCH_3 \xleftarrow{3}{-3} CCl_2FCH_2 + HCl$ | 4.37° 4.84° | 4.82 6.48 | 0.45 | 9.26 ^e 7.69 ^c | 9.09 7.81 | -0.17 |
| $\text{CCl}_2\text{FCH}_2 \cdot \xleftarrow{4}{-4} \text{CClF} = \text{CH}_2 + \text{Cl}$ | $\frac{19.97^{\circ}}{0.00^{\mathrm{f}}}$ | $\frac{20.54}{0.00}$ | | $\frac{14.89^{\circ}}{10.20^{f}}$ | $\frac{15.15}{10.37}$ | 0.17 |
| $Cl + CCl_2FCH_3 \xleftarrow{5}{-5} \cdot CClFCH_3 + Cl_2$ | $\frac{22.05^{\circ}}{2.00^{\mathrm{g}}}$ | $\frac{20.77}{1.74}$ | -0.26 | $\frac{10.51^{\circ}}{8.80^{g}}$ | <u>10.81</u> 8.99 | 0.19 |
| $\cdot \text{CCIFCH}_3 + \text{HCl} \underbrace{\stackrel{6}{\longleftarrow}}_{-6} \text{CHCIFCH}_3 + \text{Cl}$ | 9.35 ^c 2.48 ^h | $\frac{10.02}{3.07}$ | 0.59 | 8.43° 10.00 ^h | 8.09 9.95 | -0.05 |
| 2 ·CClFCH ₃ $\xrightarrow{7}$ product(s) | 0.00^{d} | 0.00 | _ | 9.30 ^d | 9.23 | -0.07 |
| $Cl + wall \xrightarrow{8} Cl$ -wall c. Additional radical reactions when CCl_4 is added | -0.08^{i} | -0.28 | -0.20 | -0.12^{i} | 0.02 | 0.14 |
| $\operatorname{CCl}_4 \xrightarrow{9} \operatorname{CCl}_3 \cdot + \operatorname{Cl}$ | $\frac{67.91^{\circ}}{0.00^{j}}$ | $\frac{68.17}{0.00}$ | | $\frac{16.77^{\circ}}{10.86^{j}}$ | $\frac{16.84}{10.76}$ | -0.10 |
| $\text{Cl} + \text{CCl}_4 \xrightarrow[-10]{} \text{CCl}_3 \cdot + \text{Cl}_2$ | $\frac{15.52^{\circ}}{5.10^{j}}$ | $\frac{15.69}{5.00}$ | -0.10 | 10.78° 8.70 ^j | 11.09 8.83 | 0.13 |
| CCl_3 + $\operatorname{CCl}_2\operatorname{FCH}_3 \xrightarrow[-11]{-11} \operatorname{CCl}_3\operatorname{H} + \operatorname{CCl}_2\operatorname{FCH}_2$ | $\frac{19.00^{k}}{11.24^{c}}$ | $\frac{19.23}{13.37}$ | 0.23 | 8.99 ^k 8.82 ^c | 8.97 9.08 | -0.02 |
| CCl_3 · + HCl $\xrightarrow{12}_{-12}$ CCl_3 H + Cl | $\frac{11.53^{\circ}}{3.30^{1}}$ | $\frac{10.88}{3.37}$ | 0.07 | 8.41° 9.80 ¹ | 8.49 9.89 | 0.09 |
| $2 \operatorname{CCl}_3 \cdot \underbrace{\xrightarrow{13}}_{-13} \operatorname{C}_2 \operatorname{Cl}_6$ | $\frac{0.00^{j}}{66.73^{c}}$ | $\frac{0.00}{67.07}$ | | 9.67 ^j 17.27 ^c | <u>9.71</u> 17.58 | 0.04 |
| CCl_3 + $\cdot CClFCH_3 \xrightarrow{14} product(s)$ | 0.00^{d} | 0.00 | _ | 9.30 ^d | 9.27 | -0.03 |

Table I Kinetic Model for the Pyrolysis of CCl₂FCH₃^a

^a The activation energies E are expressed in kcal/mol and the preexponential factors A in L, mol, and s-units: the values given below the lines are for back reactions. Initial and Optim. are values before and after optimization, respectively. Correction Corr. = Optim. – Initial. When a dash (—) is given for Corr., the corresponding parameter was held constant during the optimization.

^b Experimental value obtained by means of OPTKIN from the data of this work concerning only the experiments with added propene.

^c Calculated in the computer program from the thermodynamic data given in Table II and the rate constant of the back reaction at the mean temperature of all experiments.

^d Experimental data for the recombination reaction between Cl atoms and halogenated radicals are very scarce. It is, however, generally accepted that these reactions occur with zero activation energy and a preexponential factor of 10^{10.3} L/mol.s [1].

Recombination reactions between two halogenated alkyl radicals are expected to proceed slower. The value for the preexponential factor and the rate constant is estimated at $10^{9.3}$ L/mol.s [9].

^e Experimental value from [10].

^fAssumed to be equal to the value for $Cl + CF_2 = CH_2 \rightarrow CClF_2CH_2 \cdot$ from [11], derived from fitting to a mechanism.

^g Estimated from Arrhenius parameters for similar reactions.

^h Experimental value from [12].

ⁱ Value determined in [5] for the reactor used in this work.

^j Value derived from fitting to a mechanism in [6].

^k Assumed to be equal to the value for $CCl_3 \cdot + CClF_2CH_3 \rightarrow CCl_3H + CClF_2CH_2 \cdot \text{proposed in [2]}.$

¹Experimental value from [13].

| Compound | $\Delta H^{\circ}_{f,298}$ | | S°_{298} | | $C_{p,T}^{\circ}$ | | |
|-----------------------------------|----------------------------|-------|-------------------|-------|-------------------|----------------|---------------------|
| | Initial | Corr. | Initial | Corr. | а | $10^2 \cdot b$ | $10^{5} \cdot c$ |
| Cl | 29.0ь | | 39.5 ^b | | 4.72 | 0.225 | -0.179 ^b |
| CCl_3 · | 18.0 ^c | 0.12 | 71.2° | 0.60 | 9.87 | 2.24 | -1.41 ^b |
| ·CCIFCH3 | - 30.2 ^d | -0.43 | 68.8° | 0.89 | 4.32 | 4.35 | -1.44^{f} |
| CCl_2FCH_2 . | -29.7 ^g | -0.60 | 74.4 ^f | -0.89 | 9.5 | 3.98 | -1.11^{f} |
| Cl ₂ | 0.0 ^b | | 53.3 ^b | _ | 7.07 | 0.426 | -0.25 ^b |
| HCI | -22.1 ^h | | 44.7 ^h | _ | 7.19 | -0.114 | 0.161 ^h |
| CCl ₃ H | -24.6^{i} | -0.60 | 70.6 ⁱ | 0.59 | 7.49 | 3.12 | -1.73^{i} |
| CCl ₄ | -22.2° | -0.15 | 73.8° | -0.19 | 12.80 | 3.00 | -1.93 ^b |
| CHCIFCH ₃ | - 74.9 ^j | -0.35 | 65.8 ^k | -0.45 | 7.32 | 4.35 | -1.44^{k} |
| CCl ₂ FCH ₃ | -80.8^{j} | 0.59 | 71.4 ^k | 0.39 | 12.50 | 3.98 | -1.11^{k} |
| CCl ₃ CCl ₃ | -33.2° | -0.11 | 95.2° | -0.04 | 19.90 | 5.35 | -3.32° |
| CCIF=CH ₂ | -36.9^{1} | -0.03 | 67.4 ¹ | -0.47 | 5.69 | 3.82 | -1.87^{1} |

Table II Enthalpies of Formation ΔH_f° (kcal/mol), Heat Capacities $C_{pT}^{\circ} = a + bT + cT^2$, and Entropies S° (Gibbs/mol) Based on a 1-Atm Standard State^a

^a Initial and Optim. are values before and after optimization, respectively. Correction Corr. = Optim. – Initial. When a dash (-) is given for Corr., the corresponding parameter was held constant during the optimization.

^b From JANAF thermochemical tables [14].

^c Value derived from fitting to a mechanism in [6] and [7].

^d Estimated value which corresponds to a value of the C—Cl bond dissociation energy for CCl_2FCH_3 lying between the values for CCl_3CH_3 and $CClF_2CH_3$, calculated from data given in [1] and [3], respectively.

^eEstimated value that corresponds to a value of the preexponential factor for step (2) (see Table I) lying between those for the cases of CCl_3CH_3 [1] and $CClF_2CH_3$ [3].

^fValue for a radical *R* estimated from the value for the corresponding molecule RH from this table.

^g Obtained from an interpolation of C—H bond dissociation energies for CCl_3CH_3 and $CClF_2CH_3$, calculated from data given in [1] and [3], respectively.

^hCritical evaluation in [15].

ⁱCritical evaluation in [16].

^jEstimated value from [17].

^k Estimated by means of Yoneda's method (see [18]) from the value for CCIF₃CH₃ estimated in [5].

¹Estimated from database in [19].



Figure 1 Pyrolysis of 14.4 torr CCl_2FCH_3 at 697.8 K. Concentration *C* of $CClF=CH_2$ vs. reaction time *t*. (•)—Experimental; (Full and dotted curves)—Simulations using optimized and initial Arrhenius parameters from Table I, respectively; (Dashed curve)—Simulation using only the molecular reaction (1) and its optimized Arrhenius parameters from Table I.

ular reaction (1) and the radical reaction (3) (see Table I). The concentration of the Cl atoms thus increases rapidly with time and hence also the rate of the radical chain propagation (3), while the concentration of the unreactive radicals decreases (see, e.g., Fig. 3). The amounts of Cl₂ and CHClFCH₃, produced by steps (5) and (6), respectively, are more than a thousand times lower than that of the main product CCIF=CH₂. Nevertheless, these steps are quite quickly close to reaching a steady state of quasiequilibrium. Therefore, as can be seen from Figure 3, the unreactive radicals remain the most abundant. This figure also shows that the concentration of the $CCl_{2}FCH_{2}$ radicals is so low that these chain carriers would not be involved in chain termination steps even if "fall-off" effects would significantly decrease their dissociation rate in step (4). The small influence of the rate parameters of this chain propagation step is confirmed by sensitivity analyses as a function of reaction time. These analyses were performed with OPTKIN using the model from Table I completed with all possible chain terminations in-



Figure 2 Pyrolysis CCl_2FCH_3 . Concentration *C* of CClF == CH_2 vs. reaction time *t*. (•)—Temperature = 654.0 K and initial pressure of $CCl_2FCH_3 = 107.0$ torr; (\odot)—Temperature = 696.2 K and initial pressure of $CCl_2FCH_3 = 53.0$ torr; (Full curves)—Simulations using optimized Arrhenius parameters from Table I; and (Dashed curves)—Simulations using only the molecular reaction (1) and its optimized Arrhenius parameters from Table I.

volving the CCl₂FCH₂· radicals. For example, they reveal that for the experiment at 696.2 K from Figure 2, the reduced sensitivity coefficient $\partial(\ln[\text{CClF}=\text{CH}_2])/\partial(\ln(\text{rate constant}))$ for step (4) is about a hundred times smaller than that for the other chain propagation step (3). These analyses also show the relative importance of the molecular step (1), the chain initiation step (2), the transfer steps (5), (-5), (6), and (-6), and the termination steps (-2), (7), and (8), as well as the low sensitivity to the rate constant of the reverse steps (-1), (-3), and (-4), and of the added



Figure 3 Pyrolysis of 107.0 torr CCl₂FCH₃ at 654.0 K (see Fig. 2). Concentrations *C* of radicals and Cl atoms vs. reaction time *t*. Simulations using optimized Arrhenius parameters from Table I.



Figure 4 Pyrolysis of 200 torr CCl_2FCH_3 at 803 K. Concentration *C* of $CClF=CH_2$ vs. reaction time *t*. (•)—Calculated from experiments in [4]; (Full curve)—Simulation using optimized Arrhenius parameters from Table I; and (Dashed curve)—Simulation using only the molecular reaction (1) and its optimized Arrhenius parameters from Table I.

chain termination steps. Note also that the sensitivity coefficient for a possible isomerization of \cdot CClFCH₃ radicals to CClFHCH₂ \cdot radicals by H atom migration is very low.²

Further support for the optimized molecular-radical model is to be found in the good agreement between experimental³ and simulated concentrations of the CCIF=CH₂ product (see Fig. 4) at a temperature about 100 K higher than the highest temperature used for the optimization of the model. The molecular model prediction is not much lower (see also Fig. 4). This could explain why Sianesi et al. [4] did not observe a large inhibitory effect of added NO.

It thus seems that the molecular pathway plays a much more important role in the dehydrochlorination of CCl_2FCH_3 than that suggested in [4].

Pyrolysis of CCl₂FCH₃ in the Presence of Propene

The pyrolysis of CCl_2FCH_3 has also been studied in the presence of propene added as radical scavenger between 650 and 700 K. The pressure of CCl_2FCH_3 ranged from 15 to 120 torr and that of propene from 0.5 to 7 torr. The addition of propene slightly reduces

²The model consisted of the reactions from Table I, the isomerization, the decomposition of the produced radicals, their reactions with HCl and Cl_2 , and all possible reverse reactions and chain terminations.

³Calculated for experimental conditions from Sianesi et al. [4] (200 torr of CCl_2FCH_3 at 803 K and a reaction time of 2 s) using the rate constant measured by these authors.



Figure 5 Pyrolysis of CCl_2FCH_3 in the presence of propene. Concentration *C* of $CCIF=CH_2$ vs. reaction time *t*. (•)—Temperature = 650.8 K and initial pressures of CCl_2FCH_3 and propene = 58.2 and 1.6 torr, respectively; (•)—Temperature = 698.7 K and initial pressures of CCl_2FCH_3 and propene = 52.5 and 1.82 torr, respectively; and (Full curves)—Simulation using only the molecular reaction (1) and its optimized Arrhenius parameters from Table I.

the reaction rate and the autoacceleration disappears. The amount of C_3H_6 is of no influence. The reaction observed must therefore correspond to the maximally inhibited dehydrochlorination. It is of the first order. Its rate can thus be attributed to the homogeneous molecular elimination of HCl. The optimized values for the activation energy *E* and the preexponential factor



Figure 6 Pyrolysis of 98.3 torr CCl_2FCH_3 in the presence of 8.0 torr CCl_4 at 612.6 K. Concentration *C* of $CClF=CH_2$ vs. reaction time *t*. (•)—Experimental; (Full curve)—Simulation using optimized Arrhenius parameters from Table I; and (Dashed curve)—Simulation in the absence of added CCl_4 .



Figure 7 Pyrolysis of 48.1 torr CCl_2FCH_3 in the presence of 6.3 torr CCl_4 at 655.5 K. Concentration *C* of $CClF=CH_2$ vs. reaction time *t*. (•)—Experimental; (Full curve)—Simulation using optimized Arrhenius parameters from Table I; and (Dashed curve)—Simulation in the absence of added CCl_4 .

A are 57.05 kcal/mol and $10^{14.02}$ s⁻¹, respectively (see Table I).⁴ These values fit the experimental data very well (see Fig. 5). The value of *E* is to be compared with the values of 56.0 and 58.5 kcal/mol obtained from chemical activation experiments [21] and *ab in-itio* quantum chemical calculations [22], respectively. Note that the molecular elimination of HF has a 14 kcal/mol higher *E* [21]. This means that at a mean temperature of 675 K the ratio of concentrations [CCl₂=CH₂]/[CFCl=CH₂] should be on the order of 10^{-4} . The much higher value observed (about 10^{-1}) suggests heterogeneous rather than homogeneous HF elimination in this work.

Pyrolysis of CCl_2FCH_3 in the Presence of CCl_4

The pyrolysis of CCl_2FCH_3 has also been studied in the presence of added CCl_4 at temperatures between 612 and 656 K. The pressure ranged from 36 to 104 torr for CCl_2FCH_3 and from 2 to 8 torr for CCl_4 . Figures 6 and 7 show that in the temperature range studied, the dehydrochlorination is much faster when CCl_4 is added and that its rate also increases in the course of time. As also can be seen, this autoacceleration is well described by the optimization model. Analyses of the rates of the elementary reaction steps show that (i)

⁴Optimizations based solely on the experiments in the presence of propene yield almost the same Arrhenius parameters (see Table I); this also holds when only the experiments with pure CCl_2FCH_3 are used.

the acceleration is due to the supplementary production of Cl atoms by the fast chain initiation step (9), and (ii) the autoacceleration results from reactions (11) and (12), which convert unreactive CCl_3 · radicals into reactive CCl_2FCH_2 · and Cl chain carriers, respectively. Figure 8 shows that the concentration of the CCl_3 · radicals remains almost constant in the course of reaction, while the concentrations of the chain carriers increase. It also appears that the concentration of the CCl_2FCH_2 · radical is so low that its participation in the chain terminations is negligible. This is also true for the unreactive ·CClFCH₃ radical, except at the beginning of the reaction.

For the sake of completeness, numerical calculations show that (i) the reactions (5), (6), (10), and (12) tend rapidly towards a steady state of quasiequilibrium; (ii) the amounts of the side products Cl_2 , CHCIFCH₃, CCl₃H, and C₂Cl₆ formed in steps (10) to (13), respectively, are at least 10³ times lower than that of the reaction product CCIF=CH₂; and (iii) CCl₄ is almost not consumed in the course of the reaction.

CONCLUSION

The kinetics of the dehydrochlorination of CCl_2FCH_3 is complex. At the beginning, the radical reaction is much slower than the molecular reaction, but it accelerates and rapidly becomes equally fast. In the presence of CCl_4 , on the other hand, the radical reaction is always much faster than the molecular reaction and accelerates, too. All these observations can be quantitatively described by the model given in Table I. This



Figure 8 Pyrolysis of 48.1 torr CCl_2FCH_3 in the presence of 6.3 torr CCl_4 at 655.5 K (see Fig. 7). Concentrations *C* of radicals and Cl atoms vs. reaction time *t*. Simulations using optimized Arrhenius parameters from Table I.

model also enables one to explain why Sianesi et al. observed only a weak inhibitory effect of added NO [4] and to determine the Arrhenius parameters of the molecular dehydrochlorination even from experiments in the absence of added propene.

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