

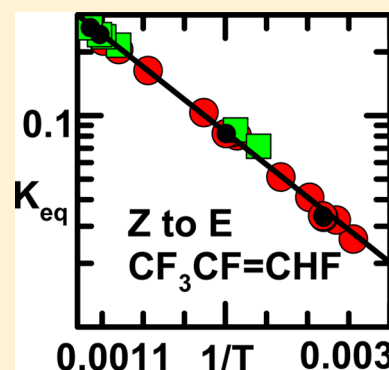


Study of the Thermodynamics (Thermal and Cl Catalyzed) and Kinetics of the Cis and Trans Isomerizations of $\text{CF}_3\text{CF}=\text{CHF}$, $\text{CF}_3\text{CH}=\text{CHCF}_3$, and $\text{CH}_3\text{CH}=\text{CHCH}_3$ in 100–950 Torr of N_2 Diluent at 296–875 K: Effect of F and CF_3 Substitution on the Isomerization Process Including the Fluorine “Cis Effect”

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ABSTRACT: The equilibrium constants for the Z to E isomerizations of $\text{CF}_3\text{CF}=\text{CHF}$ (K_1) and $\text{CF}_3\text{CH}=\text{CHCF}_3$ (K_2) have been measured using GC/FID analysis over the temperature ranges 360–850 and 297–850 K, respectively. At lower temperature, K was determined using Cl atom catalysis. At higher temperature, K was measured without a catalyst. The temperature-dependent expressions are K_1 (Z to E) = $1.45(\pm 0.15) \cdot e^{-[2845(\pm 100)/RT]}$ and K_2 (Z to E) = $1.9(\pm 0.22) \cdot e^{+[4330(\pm 120)/RT]}$ (where the gas constant $R \equiv 1.986 \text{ cal mol}^{-1} \text{ K}^{-1}$). For isomerization 1, the Z (fluorine cis) isomer is $2.85 \text{ kcal mol}^{-1}$ lower in energy than the E (fluorine trans) isomer, providing another example of the fluorine “cis effect” in olefins. For isomerization 2, the E(trans) isomer is $4.3 \text{ kcal mol}^{-1}$ lower in energy than the corresponding Z(cis) isomer as is normal for olefins. The isomerization rate constant in a single direction was also measured for each fluorinated compound: k_{-1} (E to Z) = $10^{13.87 \pm 0.24} \cdot e^{-59530(\pm 887)/RT} \text{ s}^{-1}$; and k_2 (Z to E) = $10^{13.89 \pm 0.23} \cdot e^{-58845(\pm 675)/RT} \text{ s}^{-1}$. To verify the experimental method, cis to trans (k_3) and trans to cis (k_{-3}) isomerization rate constants were also measured for *cis*- and *trans*-2-butene for comparison to several previous studies. The rate constants determined herein are k_3 (cis to trans) = $10^{13.95 \pm 0.23} \cdot e^{-63245(\pm 815)/RT} \text{ s}^{-1}$; and k_{-3} (trans to cis) = $10^{14.32 \pm 0.28} \cdot e^{-64993(\pm 1132)/RT} \text{ s}^{-1}$. k_3 agrees well with four previous measurements and represents the best available rate constant for 2-butene. All errors quoted here are 2σ . The typical total pressure for these experiments was $760 \pm 100 \text{ Torr}$. Limited experiments performed at 100 Torr showed no pressure dependence for any of the compounds above 100 Torr. Thus, all isomerization rate constants represent high-pressure limits. The rates of the addition reactions of Cl to the double bonds of $\text{CF}_3\text{CF}=\text{CHF}$ (k_4) and $\text{CF}_3\text{CH}=\text{CHCF}_3$ (k_7) (used in Cl catalysis) were also measured in pure N_2 and in pure O_2 . In O_2 , the rate constants expressions are $k_4 = 1.56 (\pm 0.22) \times 10^{-11} \cdot e^{+(643/RT)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; and $k_7 = 1.05 \times 10^{-12} \cdot e^{+(1874/RT)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In N_2 , k_4 and k_7 decrease several orders of magnitude as the temperature increases because of the increasing reversibility of the Cl addition reaction, which produces the catalytic effect.



1. INTRODUCTION

Experiments more than 50 years ago measured the enthalpy of the cis to trans isomerization of 1,2-difluoroethylene. The results were surprising because for this molecule the cis isomer was lower in energy than the trans.^{1,2} This finding was labeled the “cis effect,”² and that description has been adopted by authors of more recent publications.^{3–7} This effect has been shown to occur with halogen substituents other than fluorine.² The result is contrary to “typical” cis–trans isomerizations such as that of 2-butene, where the trans isomer is lower in energy because of steric interaction between the CH_3 groups. Over the years a number of ab initio calculations, beginning with that of Binkley and Pople,⁸ have been carried out, particularly focusing on the structure and energetics of 1,2-difluoroethylene. Many of these studies, exemplified by the high-level calculations of Feller et al.,⁴ agree that the cis isomer is lower in energy than the trans isomer. An understanding of why this is so remains elusive. A detailed discussion of these extensive theoretical studies is beyond the scope of this paper, but valuable

summaries can be found in these publications and the references therein.^{3–7,9}

One of us (E.W.K.) carried out experiments on the kinetics and thermodynamics of the trans to cis isomerization of octafluoro-2-butene.¹⁰ In this case, the trans isomer is $\sim 800 \text{ cal mol}^{-1}$ lower in energy than the cis even though, in the cis isomer, F atoms are located cis to one another across the double bond. The reasonable postulate was made that this occurred because the steric repulsion of the relatively large CF_3 groups more than counteracted the stabilizing “cis effect” of the two fluorine atoms located on the double bond. However, no additional experiments were carried out to verify this postulate. Because of the continuing interest in the fluorine “cis effect” from a theoretical perspective and the lack of extensive experimental data probing this effect, we have undertaken

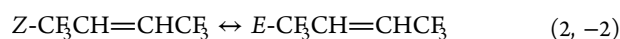
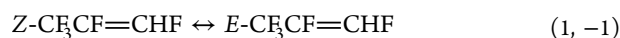
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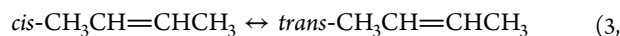


both thermodynamic and kinetics measurements on the *cis*/*trans* isomerizations of two additional fluorinated alkenes, $\text{CF}_3\text{CF}=\text{CHF}$ and $\text{CF}_3\text{CH}=\text{CHCF}_3$. Both the enthalpies and rate constants of the isomerizations of $\text{CF}_3\text{CF}=\text{CHF}$ (reaction 1) and $\text{CF}_3\text{CH}=\text{CHCF}_3$ (reaction 2) are presented herein. The



experiments on $\text{CF}_3\text{CF}=\text{CHF}$ provide data on another molecule that could exhibit the “*cis* effect” of 1,2-fluorine substitution at a carbon–carbon double bond. The study of the isomerization of $\text{CF}_3\text{CH}=\text{CHCF}_3$ provides a measurement of the steric interaction between CF_3 groups attached on opposite ends of a carbon–carbon double bond that will allow improved interpretation of the octafluoro-2-butene data presented in ref 10. Measurement of the rate constant of the *cis*/*trans* isomerization of $\text{CHF}=\text{CHF}$ would have been useful because it has only been studied twice by the same research group, yielding significantly different activation energies as will be discussed later. Unfortunately, this compound was not available commercially while the current experiments were being conducted, and this discrepancy could not be explored.

In addition, we present measurements of the rate constants of the *cis*/*trans* isomerizations of 2-butene (reactions 3, –3). This molecule has been studied extensively and is used here as a test of the experimental technique and a verification of the calibration of the temperature measurement



The current measurements produced a rate constant for the *cis* to *trans* reaction which agrees with previous measurements over the temperature range 680–1200 K and is arguably the best rate constant for this reaction to date.

At temperatures in excess of 700 K, both the enthalpy of reaction and rate constant for isomerization of the fluorocarbons are measured in mixtures of the desired reactants in N_2 diluent with no catalyst present. At lower temperatures, the isomerization reaction becomes very slow, and the equilibrium constants are obtained using Cl atom catalysis in mixtures containing the reactant, Cl_2 , and a bath gas. Cl atoms are generated from Cl_2 by continuous UV photolysis using a fluorescent lamp. GC/FID analysis is used to measure the mole fractions of reactants and products. The Cl atoms react reversibly with $\text{CF}_3\text{CF}=\text{CHF}$ to form two possible chloroalkyl radicals



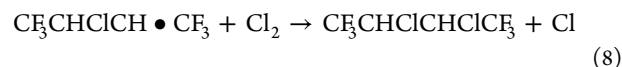
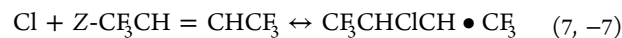
The alkyl radicals formed in reaction 4 subsequently react with Cl_2 present in the initial mixture to form a dichloride ($\text{CF}_3\text{CFCICHFCl}$) in the absence of O_2 via the irreversible reactions



If O_2 is present in the reacting mixture, the chlorinated radicals formed in reaction 4 can also react with O_2 by reactions 6a and 6b. These reactions are irreversible at lower temperatures



Similar reactions occur for $\text{CF}_3\text{CH}=\text{CHCF}_3$ except in this case there is only one radical species



formed by Cl addition. This radical can react also with O_2 .

Initially, this experiment was designed to measure the kinetics and products of the reaction of Cl with $\text{CF}_3\text{CF}=\text{CHF}$. During the course of this research, we realized that these experiments could shed light on the “*cis* effect”. By using Cl atom catalysis to promote *cis*–*trans* isomerization at a relatively low temperature, accurate measurement of the enthalpy of isomerization for $\text{CF}_3\text{CF}=\text{CHF}$ could be obtained.

The classic technique for catalyzing *cis*–*trans* isomerization in an olefin is to use iodine atom addition to the double bond.¹ The iodoalkyl adduct formed uncouples the double bond allowing rotation to occur about a now single bond. The iodoalkyl radical is relatively unstable with respect to loss of the iodine atom and, when it decomposes, it can form either the *trans* or *cis* isomer of the olefin, thereby catalyzing the isomerization. Our experiment was set up to use Cl atoms, and in order to assess the suitability of Cl atoms as a catalyst in the isomerization process, the rate constant and the mechanism of Cl addition to both $\text{CF}_3\text{CF}=\text{CHF}$ and $\text{CF}_3\text{CH}=\text{CHCF}_3$ were investigated in detail. These results are included as separate, self-contained sections (sections 3.2.1 and 3.3.1) herein. These sections demonstrate that Cl can catalyze the isomerizations effectively by a mechanism analogous to that described for iodine atoms.

2. EXPERIMENTS

The GC/FID analysis has been described in detail in ref 11. The primary GC column was the 30m DB-1 described in this reference. However, this column did not separate the $\text{CF}_3\text{CF}=\text{CHF}$ isomers completely. For that reason, several experiments were carried out on $\text{CF}_3\text{CF}=\text{CHF}$ using a 10 m \times 0.32 mm GS-GasPro column (isothermal at 100 °C), which provided better separation. The results from both columns were indistinguishable. A spherical (500 cm^3) Pyrex reactor, equipped with a Teflon-sealed Pyrex stopcock, was used for ambient-temperature measurements. The experiments were performed using initial mixtures (prepared by partial pressure in a vacuum manifold) of Cl_2 (purity = 99.7%), the species under study, and a kinetic reference species if a Cl rate constant is being determined using the relative rate method, diluted by N_2 (99.999% min) or O_2 (99.998%). The mixtures were prepared by partial pressure measurement using a vacuum manifold. The fluorocarbon reactant purities were *Z*- $\text{CF}_3\text{CF}=\text{CHF}$ (99%), *E*- $\text{CF}_3\text{CF}=\text{CHF}$ (96.5%), *E*- and *Z*- $\text{CF}_3\text{CH}=\text{CHCF}_3$ (97%), and *E*- and *Z*-2-butene (99%). All fluorocarbons were purchased from Synquest Laboratories, Inc. with the exception of *Z*- $\text{CF}_3\text{CF}=\text{CHF}$ which was provided by Rajiv Singh of Honeywell Laboratories. Either C_2H_6 (99.999%), $\text{C}_2\text{H}_5\text{Cl}$ (99.5%), CH_3Cl (99.5%), CFCl_2H (99%), or HFC 134a (CF_3CFH_2 , 99%) was added as a reference compound in the relative rate experiments to measure the dependence of the overall rate coefficient for reactions 4 and 7 on temperature and O_2 mole fraction. The rate constants for these reference

Table 1. Initial Conditions and Rate Constants for All Thermal Z(Cis) to E(Trans) and Selected E to Z Isomerizations of CH₃CH=CHCH₃ in N₂ Diluent, Whose Rate Constants Are Plotted in Figure 1

Z to E Isomerization												
data	t^a (s)	T (K)	P (Torr)	Z_0^b (ppm)	E_0^b (ppm)	Z_t^b (ppm)	E_t^b (ppm)	$[(Z + E)_t]/[(Z + E)_0]^c$	E_t/Z_t	K_3^d calcd	Z_{eq}^d (ppm)	k_3^e (s ⁻¹)
1a	1830	751	760	450	1	422	29	0.985	0.069	1.36	191	3.58×10^{-5}
1b	3600	753	760			392	59	0.974	0.151	1.36	191	4.07×10^{-5}
1c	19 440	755	760			257	194	0.832	0.755	1.36	191	4.04×10^{-5}
1d ^f	60 660	755	740			198	253	0.144	1.278	1.36	191	3.45×10^{-5}
2a	82	816	760	500	1.3	462	39	0.976	0.844	1.32	216	9.98×10^{-4}
2b	373	816	770			364	137	0.940	0.376	1.32	216	9.90×10^{-4}
3a	74	841	760	399	1	323	77	0.964	0.238	1.307	173	3.13×10^{-3}
3b	156	841	750			266	134	0.927	0.504	1.307	173	3.24×10^{-3}
3c	362	841	760			200	200	0.801	1.00	1.307	173	3.30×10^{-3}
4	53	874	820	513	1.3	302	212	0.890	0.702	1.290	223	1.39×10^{-2}
E to Z Isomerization												
data	t^a (s)	T (K)	P (Torr)	Z_0^b (ppm)	E_0^b (ppm)	Z_t^b (ppm)	E_t^b (ppm)	$[(Z + E)_t]/[(Z + E)_0]^c$	Z_t/E_t	K_{-3}^d calcd	E_{eq} (ppm)	k_{-3}^e (s ⁻¹)
5a	1770	771	760	0.3	443	53	390	0.979	0.120	0.741	254	7.88×10^{-5}
5b	5430	771	760			117	326	0.934	0.359	0.741	254	7.55×10^{-5}
6a	45	816	720	0.5	423	15	408	0.979	0.037	0.757	241	7.93×10^{-4}
6b	391	816	760			92	332	0.949	0.277	0.757	241	7.67×10^{-4}
6c	1210	816	770			163	262	0.734	0.622	0.757	241	7.68×10^{-4}
6d	410	817	170			94	330	0.960	0.285	0.757	241	7.53×10^{-4}
7a	51	843	720	0.5	411	52	359	0.962	0.145	0.743	236	2.92×10^{-3}
7b	250	843	750			143	269	0.901	0.532	0.743	236	2.84×10^{-3}
7c	147	843	118			108	304	0.971	0.355	0.743	236	2.74×10^{-3}
8a	33	875	720	0.3	337	85	253	0.950	0.336	0.775	190	1.12×10^{-2}
8b	57	875	770			122	215	0.904	0.567	0.775	190	1.35×10^{-2}
8c	192	876	780			145	192	0.731	0.755 ^g	0.775	190	
8d	547	876	680			147	191	0.336	0.770 ^g	0.775	190	

^aTime in reactor. ^bInitial (0) and final (t) reactant mole fractions. Final mole fractions are corrected for decomposition loss (see text). ^cRatio of total final to initial 2-butene mole fraction (labeled fractional recovery in section 3.1) showing decomposition loss. ^dEquilibrium constants (K_3 and K_{-3}) at temperature T calculated from ref 17. $Z_{eq} = (Z_0 + E_0)/(1 + K_3)$; $E_{eq} = (Z_0 + E_0)/(1 + K_{-3})$. ^eRate constant for reaction 3, -3. These are the values used in generating Figure 1. Values calculated using the mole fractions in the table may deviate slightly because of round off. ^fNot used in Figure 1 since this data point is near equilibrium. ^gExperimental measurement of K_{-3} . The Z_t/E_t values at 192 s (8c) and 547 s (8d) are equal indicating equilibrium.

compounds are presented in the Appendix. Freeze/thaw degassing cycles were performed on all condensable reactants. In addition, CF₂Cl₂ (99%) was included in the reaction mixtures for internal calibration of the GC samples. This molecule does not react with Cl and is thermally stable at the maximum temperature/reaction time of these experiments as discussed in the Appendix.

Chlorine atoms were formed by irradiation of the unreacted mixture with UV light peaking near 360 nm generated by a single Sylvania F6T5 BLB fluorescent lamp. This radiation dissociates the molecular chlorine to form Cl atoms in their ground state. At ambient temperature after a chosen irradiation time, 1 cm³ of the contents of the 500 cm³ reactor was removed into a 2.5 cm³ gastight syringe (Hamilton) using the vacuum manifold and analyzed by direct injection of this sample into the injector port (373 K) of the gas chromatograph. The presence of the internal calibration species permitted corrections to be made for uncertainty in the precise amount of sample injected into the GC using the syringe. The mixture in the 500 cm³ reactor was then irradiated for additional times, and additional analyses were performed. All ambient temperature experiments in this reactor were carried out at a total pressure of 800–950 Torr. Typical reactant partial pressure ranges are presented in subsequent sections.

Elevated temperature experiments were performed over the range 297–875 K using a ~40 cm³, cylindrical, Pyrex reactor (26 mm i.d. \times ~7 cm length) with a thermocouple well along the axis and a Teflon-sealed, glass stopcock attached to a Pyrex capillary tube at the end opposite the thermocouple well. This reactor was placed inside a tube oven, whose lid remained open approximately 6 mm to allow radiation from the fluorescent lamp to enter. The calibration of the chromel–alumel thermocouple was checked in ice, boiling water, and hot oil, whose temperature was measured by a calibrated thermometer. The temperature along the axis of the reactor was uniform to ± 2 –3 K from the mean at temperatures above 650 K and ± 1 K for temperatures of 550 K and below. In addition, the temperature was measured once by a second chromel–alumel thermocouple at 450 K. The temperature reading of both thermocouples agreed to within 1 K. Calibration at temperatures above 550 K was not available. During a reaction, a portion of the unreacted mixture was placed into the high-temperature reactor at pressures varying from 100 to 800 Torr using the vacuum manifold connected to the reactor. When Cl₂ was present in the mixture, the mixture was then irradiated for a chosen time, and a sample of the contents was withdrawn into the gastight syringe after removing a small amount to purge the low-temperature dead volume. Only one irradiation was

possible per sample placed into the reactor for the high-temperature experiments because of pressure loss during sampling into the gastight syringe using the vacuum manifold. For experiments in which no Cl_2 is present, no irradiation is applied. The sampling time into the syringe is very rapid, quenching any thermal reactions that are occurring. The photolytic reactions stop when the UV lamp is turned off. Although room light produces no measurable Cl_2 dissociation, in an abundance of caution, the syringe and the Pyrex vacuum vessel holding the unreacted mixture are both covered with aluminum foil to exclude light. In addition, the room lights are dimmed during the experiments.

Identification and calibration of the reactants and products were carried out by injecting a known concentration of a pure species into the GC in the presence of an internal calibration species. The calibration mixtures were prepared in Pyrex vacuum flasks by partial pressure using the vacuum manifold. This provides a determination of the FID sensitivity and retention time of the species. In the $\text{CF}_3\text{CF}=\text{CHF}$ experiments, pure samples of $\text{CF}_3\text{CFCICHFCI}$ (97%) and CF_3COF (95%) were available for identification and calibration. $\text{CF}_3\text{CFCICHFCI}$ is the sole product expected to be formed in the absence of O_2 . CF_3COF is a major product expected to form in 100% molar yield in the presence of O_2 . No product measurements were carried out during the studies of reaction 7. The GC sensitivities of the *E* and *Z* isomers of all reactants were identical to within the experimental error of $\sim 1.5\%$.

2.1. Sample Stability in the Gastight Syringe. In a typical experiment, the irradiated sample stayed in the syringe for ~ 20 s. A comparison test was run in which the sample remained in the syringe for 20 min. There was no change in the measured species concentrations to within the typical $\pm 1.5\%$ experimental error. On the basis of these results, the syringe sampling does not introduce significant error.

3. RESULTS

3.1. Isomerization of 2-Butene. The *Z* to *E* (cis to trans) and *E* to *Z* (trans to cis) isomerization rate constants were measured for 2-butene over the temperature range 750–875 K. These experiments were carried out to verify both the kinetics measurement technique and the average reactor temperature determined from the thermocouple profile by comparing our rate constants to literature values.^{12–15} In these experiments, the mixture contained only a 2-butene isomer, the internal GC calibration species (CF_2Cl_2), and N_2 diluent. The thermal stability of CF_2Cl_2 , the internal calibration species, will be discussed in the Appendix.

Table 1 presents all of the data points obtained for the *Z* to *E* isomerization, and a selection representing more than half of the data for the *E* to *Z* isomerization which appear in Figure 1. The data in the table are gathered into groups. Those with the same number but different letter designations are experiments with the same initial mixture but different residence times or pressures in the high-temperature reactor. In these 2-butene experiments, no irradiation is present. The reaction starts when the mixture is injected and ends when the sample is withdrawn from the reactor into the gastight syringe. Table 1 presents all of the data necessary to calculate the isomerization rate constants using the expression for a reversible first order reaction where the initial product mole fraction is zero. In the case of the *Z* to *E* isomerization reaction 3, the pertinent equations are¹⁶

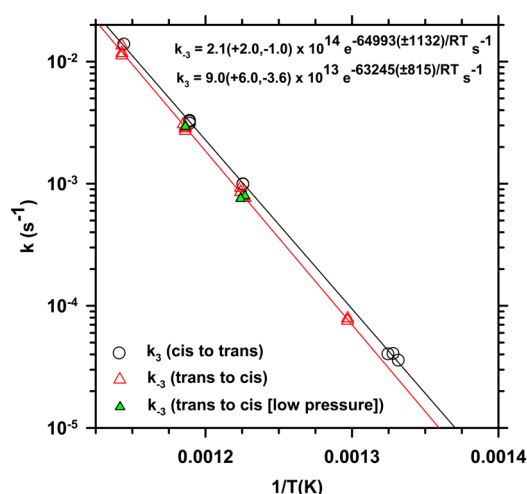


Figure 1. Rate constants at 760 Torr of N_2 for the cis to trans (k_3 , black circles) and trans to cis (k_{-3} , red triangles) isomerizations of 2-butene are plotted as functions of inverse temperature. The green filled triangles were obtained from experiments 6d and 7c in Table 1 for the trans to cis isomerizations at 170 and 118 Torr, respectively. Rate expressions for k_3 and k_{-3} are shown.

$$\ln\{([Z]_0 - [Z]_{\text{eq}})/([Z]_t - [Z]_{\text{eq}})\} = (k_3 + k_{-3})t \quad (\text{A})$$

$$k_3 = (k_3 + k_{-3})/\{1 + (1/K_3)\} \quad (\text{B})$$

$$Z_{\text{eq}} = Z_0/(1 + K_3) \quad (\text{C})$$

In these equations, the subscripts 0 and *t* represent the initial mole fraction of the reactant in the starting mixture and the final mole fraction after time *t* in the reactor, respectively. $K_3 = E_{\text{eq}}/Z_{\text{eq}}$ (where the eq subscripts denote the equilibrium mole fractions of the *Z* and *E* isomer) is the equilibrium constant for the *Z* to *E* isomerization reaction 3. The value of K_3 at each temperature was obtained from ref 17 and was checked at one temperature during the current experiments. For 2-butene, E_0 was essentially zero, and the above equations are exact. The equations for *E* to *Z* isomerization can be obtained by proper substitutions of the *E* mole fractions into eqs A–C.

From an examination of Table 1, one feature is apparent. As the time in the reactor increases (for example data points 1a–1d), not only does the *Z* to *E* isomerization progress as shown by the increase in the ratio E_t/Z_t but also the total fractional recovery of the 2-butene isomers $\{(Z + E)_t/(Z + E)_0\}$ decreases. If solely isomerization were occurring, this ratio would remain constant at unity as the reaction progresses. This decrease is caused by decomposition reactions occurring in parallel with the isomerization as has been observed previously.^{12,13,15} In carrying out the calculations of k_3 or k_{-3} , we have assumed that this parallel reaction path occurs at the same rate for both isomers and that, by dividing the observed Z_t and E_t mole fractions by the fractional recovery $\{(Z + E)_t/(Z + E)_0\}$ for each experiment to correct for this parallel loss channel, we can arrive at accurate values of k_3 and k_{-3} . The values of Z_t and E_t presented in Table 1 have been corrected for the parallel decomposition in this way. As an example, for data point 1c, the observed, uncorrected mole fractions are $Z_t(\text{uncorrected}) = 213.8$ and $E_t(\text{uncorrected}) = 161.4$ ppm.

A calculation was performed to assess the validity of this method of correcting for the parallel decomposition process.

Using the multireaction, chemical kinetics solver Acuchem,¹⁸ a four-reaction test mechanism was entered into the solver:



This reaction mechanism describes the assumptions presented above, with *Z* and *E* decomposing to the product *P*. The isomerization reaction is occurring in parallel with the decomposition reaction, which has identical rate constants for both isomers. Note that this test mechanism assumes a first order decay for the decomposition, which is a simplification since the decomposition actually occurs by a complex process. However, as long as the decomposition process occurs in parallel and does not cause isomerization, the details of the decomposition channel will not matter. The rate constants k_3 and k_{-3} were set equal to those measured in data points 1a–1c, and k_p was chosen to provide a net consumption of $(Z + E)_t$ similar to that observed from the experimental fractional recovery. From the resultant time dependent values of Z_t derived by Acuchem, the value of k_3 was determined from equations A–C by dividing the predicted Z_t by the predicted fractional recovery $\{(Z + E)_t / (Z + E)_0\}$ derived from the model. This value of k_3 was found to be identical to the input value of k_3 in the Acuchem calculation. This sample reaction mechanism verifies that under the assumptions described above this method of correction for the loss by decomposition leads to the correct result at widely varying values of the fractional recovery.

Data points 1a–1d also support experimentally the validity of this correction and the assumptions made. As the reaction time increases through this series, the magnitude of the correction factor for fractional recovery, $1/\{(Z + E)_t / (Z + E)_0\}$, becomes larger (1.015 to 6.9). Even over this large range, the isomerization rate constant calculated from the corrected data remains the same to within experimental error for this series of points, as required if the correction is valid. Data point 1d was not used in Figure 1 because it is nearing equilibrium although the value of k_3 is consistent with the others at this temperature. Taken as a whole, these checks of the correction factor verify its validity, and the measurements will yield accurate rate constants for the isomerization reaction.

Points 6d and 7c for the *E* to *Z* isomerization, obtained at reduced pressure at two temperatures, yield rate constants indistinguishable from those near 1 bar, verifying that at these temperatures the reaction is at its high-pressure limit by ~100 Torr to within experimental error. This is consistent with earlier experiments.¹² A single experimental determination of the equilibrium constant, K_{-3} , was obtained during these experiments from data points 8a–8d at 876 K. Table 1 shows that the ratio Z_t/E_t rises as the residence time in the reactor increases from 33 to 192 s. The ratio then remains constant when the residence time is tripled to 547 s. The fact that Z_t/E_t becomes constant indicates that equilibrium has been reached at a value of $K_{-3} = 0.77$. This is identical within the error of our measurements to the equilibrium constant ($K_{-3} = 0.775$) derived at 876 K from the parametric fit in ref 17. The values of K_{-3} derived from this reference are included in Table 1 and are used in calculating the rate constants. In the next section, equilibrium constants for $\text{CF}_3\text{CF}=\text{CHF}$ are determined at lower temperatures to obtain very accurate enthalpies of reaction using Cl atom catalysis. Cl catalysis was not possible

for 2-butene because it undergoes a fast Cl reaction abstracting H from the CH_3 groups, which removes all of the 2-butene long before equilibrium is reached.

Figure 1 presents Arrhenius plots of the measured *Z*(cis) to *E*(trans) and *E* to *Z* rate constants determined in the current 2-butene experiments. The rate constant expressions derived from the plots are $k_3 = 9.0(+6.0, -3.6) \times 10^{13} e^{-63245(\pm 815)/RT} \text{ s}^{-1}$, and $k_{-3} = 2.1(+2.0, -1.0) \times 10^{14} e^{-64993(\pm 1132)/RT} \text{ s}^{-1}$. The error limits quoted represent 2σ . The value of the gas constant used in these calculations is $R = 1.986 \text{ cal mol}^{-1} \text{ K}^{-1}$. These rate constant expressions can also be used to calculate a value of the equilibrium constant K_{-3} for the *E* to *Z* isomerization at 876 K for comparison to our directly measured value (data 8c and 8d in Table 1, $K_{-3} = 0.77$) presented above. $K_{-3}(876 \text{ K}) = k_{-3}/k_3 = 0.01253/0.01466 = 0.855$. This result calculated from the rate constant expressions is consistent with the directly measured value, which is more precise.

Figure 2 compares four previous measurements^{12–15} with the expression for k_3 presented here (dashed line and open circles =

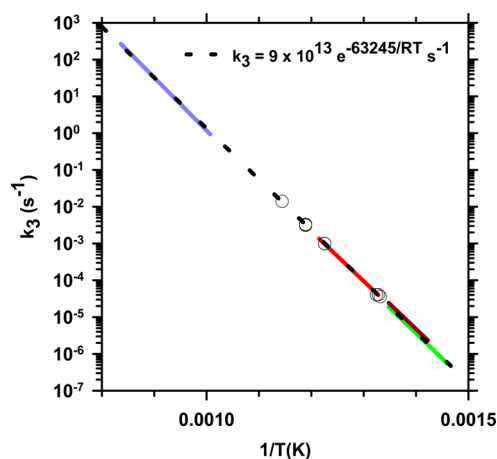


Figure 2. Comparison of the measured high-pressure rate constants for the cis to trans isomerization of 2-butene over the temperature range 680–1200 K. Blue line = Jeffers,¹⁴ green line = Rabinovitch and Michel,¹² red line = Masson et al.,¹⁵ brown line = Cundall and Palmer.¹³ The dashed line and open circles are the data and fit to the data for the cis to trans isomerization in Figure 1. The agreement among all measurements is excellent.

current data). The rate constants in refs 12, 13, and 15 are absolute measurements while that of ref 14 is a shock tube relative rate determination using the high-temperature decomposition rate constant of cyclohexene as reference. We have adjusted the rate constant expression of Jeffers¹⁴ to reflect a slight change in the best currently available rate constant of cyclohexene decomposition (see Table 3, line 2 of ref 19) [$k(\text{cyclohexene}) = 10^{15.15} e^{-33500/T}$]. In Figure 2, the lines representing the other authors' determinations of k_3 are calculated from their Arrhenius expressions at the extremes of the temperature ranges studied. The measurements in Figure 2 span a temperature range 680–1200 K and a rate constant range of 9 orders of magnitude. The rate constant k_3 derived in our experiments fits all data to better than 10% over the entire temperature range. The excellent agreement between the current and past measurements provides strong evidence that our reactor temperature profile, experimental technique, and analysis methods are correct. We believe that the value of k_3 derived from the current experiments represents the best

available rate constant for the cis to trans isomerization of 2-butene over the temperature range 680–1200 K, on the basis of its excellent fit to all available data shown in Figure 2.

3.2. Isomerization of $\text{CF}_3\text{CF}=\text{CHF}$. **3.2.1. Rate Constant of the Cl Addition Reaction.** In order to determine the equilibrium constant over a wide temperature range, a catalyst is required to obtain values at low temperatures because the uncatalyzed reaction is slow at lower temperatures. In an earlier experimental investigation of the Cl atom addition to $\text{CF}_3\text{CF}=\text{CH}_2$,²⁰ the Cl addition rate constant in N_2 diluent was observed to have a strong negative temperature dependence in relative rate experiments. This negative temperature dependence occurred because the adduct radical was not stable with respect to decomposition back to reactants. Even at room temperature some back reaction occurred. Addition of O_2 to the mixture trapped the chlorofluoroalkyl radicals as stable peroxy adducts, and the measured Cl addition rate constants increased dramatically, verifying the relative instability of the Cl adduct in N_2 diluent at the Cl_2 mole fractions present in the mixture. The relatively low stability of the Cl adduct was consistent with calculations by Papadimitriou et al.²¹ who showed that the exothermicity of the two possible Cl addition reactions to the double bond was relatively small at 14.4 and 18.7 kcal mol⁻¹.

Papadimitriou et al.²¹ also calculated the exothermicity of reactions 4a and 4b, the Cl addition to $\text{CF}_3\text{CF}=\text{CHF}$, to be 16.1 and 17.9 kcal mol⁻¹, respectively. This suggests that these chloroalkyl radicals also will be unstable at moderately elevated temperature, and, therefore, Cl atoms should function as an efficient isomerization catalyst. The double bond is broken in the initial addition process. Rotation can then occur about the now carbon–carbon single bond, and then the double bond reforms as the Cl leaves, yielding back the reactant, pentafluoropropene, either in its original or its isomerized state.

Cl addition to $\text{CF}_3\text{CF}=\text{CHF}$ and the subsequent reactions of the primary and secondary alkyl radicals with Cl_2 and O_2 are summarized as reactions 4–6 presented above. The two major products that we quantified in the current Cl + $\text{CF}_3\text{CF}=\text{CHF}$ experiments are a dichloride, $\text{CF}_3\text{CFCICHFCl}$, formed by reaction 5a or 5b in N_2 diluent and CF_3COF formed in O_2 diluent. CF_3COF is formed by a reaction sequence that is very similar to the reaction paths described in detail in ref 20 for the same product species. One other feature observed in the $\text{CF}_3\text{CF}=\text{CH}_2$ experiments was that the chlorofluoroalkyl radicals formed by Cl addition to the double bond reacted 300 times faster with O_2 than with Cl_2 at 300 K and 100 times faster at 420 K. This makes the product yields very sensitive to an O_2 contamination as small as 15–20 ppm, a level that is impossible to avoid in our experiments. Figure 3 shows the mole fractions of the $\text{CF}_3\text{CFCICHFCl}$ and CF_3COF products plotted as a function of Z- $\text{CF}_3\text{CF}=\text{CHF}$ consumed in the mixture labeled 1a–1f in Table 2 at 297 K. This mixture has no added O_2 , but the O_2 product CF_3COF is generated early from a small O_2 contaminant in the mixture. Initially, little of the dichloride product is generated but CF_3COF is formed in approximately 100% molar yield. After the O_2 is consumed, the dichloride rises linearly with ~100% molar yield and the CF_3COF generation stops. The magnitude of the O_2 contaminant can be estimated to be ~40 ppm from the concentration at which the CF_3COF generation stops and the dichloride begins to rise sharply, assuming that one O_2 is consumed per $\text{CF}_3\text{CF}=\text{CHF}$ lost. Since there is 2650 ppm of Cl_2 in the mixture (see Table 2), this shows that $k_6/k_5 > 2650/$

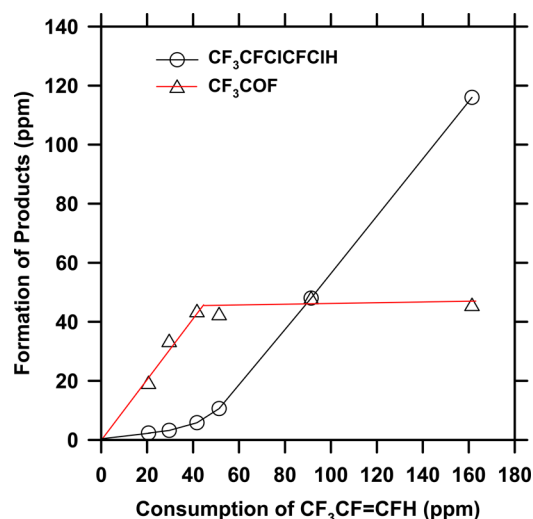


Figure 3. Yields of two major products formed during the reaction of Cl with Z- $\text{CF}_3\text{CF}=\text{CHF}$ in 760 Torr of N_2 at 297 K. These data are from experiments 1a–1f in Table 2.

40 = 66. This is consistent with the detailed measurements on the chlorofluoroalkyl radicals formed from $\text{CF}_3\text{CF}=\text{CH}_2$, which react 300 times faster with O_2 than Cl_2 at ambient temperature.²⁰ Detailed measurements of k_6/k_5 were not performed in the case of $\text{CF}_3\text{CF}=\text{CHF}$. Because the yield of the dichloride is 100% after consumption of the O_2 contaminant, we can also rule out the occurrence of significant polymerization-type reactions such as $\text{CF}_3\text{CFCICHF}(\bullet) + \text{CF}_3\text{CF}=\text{CHF}$ or any other parallel side reactions of the chlorofluoroalkyl radicals.

In order to quantify the $\text{CF}_3\text{CFCICHFCl}$ yield accurately, the effect of secondary consumption of this species by Cl must be considered. No measurements were made of this rate constant. However, the rate constant of the reaction $\text{Cl} + \text{CF}_3\text{CFCICH}_2\text{Cl}$ was measured in ref 20 ($k_a = 8.2 \times 10^{-12} \text{ e}^{-4065/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The rate constant for the abstraction reaction $\text{Cl} + \text{CF}_3\text{CFCICHFCl}$ (k_b) will be slower because there is only one H atom in the molecule and substitution of F for a hydrogen atom typically slows this type of reaction even more. At 297 K, $k_b < k_a = 8.3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This rate constant will be too slow to cause measurable secondary consumption of $\text{CF}_3\text{CFCICHFCl}$ in our experiments because k_4 is much too fast at ambient temperature ($\sim 4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). As will be seen in the discussion of Table 2, only at the highest temperature studied is secondary consumption of this product possibly present.

While we did not pursue the topic, we did observe what we believe to be the meso and chiral stereoisomers of $\text{CF}_3\text{CFCICHFCl}$ formed during reaction 5. Using the DB1 column in isothermal mode at 29 °C to improve peak separation, the dichloride GC peak showed a broadening with a shoulder on the longer retention time side. On the GasPro column, the two stereoisomers were separated into a doublet with a valley between that was approximately one-third of the height of peaks. The identity of the stereoisomers could not be determined because the individual stereoisomers are not available nor are their physical properties such as boiling points known. However, these peaks were similar in size and the pattern was very similar to that observed in the $\text{CF}_3\text{CFCICHFCl}$ calibration sample purchased from Synquest Laboratories.

Table 2. Results and Initial Conditions for Selected Experiments (Data at 300 K are in the 500 cm³ Reactor) To Determine the Enthalpy of Isomerization of CF₃CF=CFH and Its Reaction Rate Constant with Cl

data	t_{irr}^a (s)	T (K)	P (Torr)	Cl_2^b (ppm)	O_2^b (ppm)	ref_0^b (ppm)	Z_0^b (ppm)	E_0^b (ppm)	$[(Z + E)_0]/[(Z + E)_{\text{ref}}]^a$	E_0/Z_0	E_i/Z_i^c	$k_4(\text{eff})^d$	RCl_2^e (%)
1a	1	297	950	2648	none	106	337	2.9	0.957	0.0086	0.0085	4.19×10^{-11}	11
1b	2					C ₂ H ₆			0.913		0.0086	4.13×10^{-11}	11
1c	4								0.877		0.0086	4.13×10^{-11}	14
1d	6								0.849		0.0085	3.99×10^{-11}	21
1e	10								0.731		0.0091	3.95×10^{-11}	53
1f	15								0.525		0.0091	3.99×10^{-11}	72
									av = 4.06 ± 0.18				
2a	2	297	950	2490	none	139	11.4	298	0.955	26.1	25.6	4.39×10^{-11}	16
2b	4					C ₂ H ₆			0.907		25.1	4.85×10^{-11}	18
2c	8								0.872		21.0	4.02×10^{-11}	37
2d	16								0.650		18.1	4.25×10^{-11}	74
									av = 4.38 ± 0.6				
3a	23	297	950	2326	10 ⁶	104	361	3	0.908	0.0084	0.0086	4.49×10^{-11}	0
3b	262					C ₂ H ₆			0.221		0.0070	4.43×10^{-11}	0
4a	40	454	760	2559	none	1618	10.9	282	0.616	25.8	0.068	8.6×10^{-13}	69
4b	90					CFCl ₂ H			0.215		0.073	7.2×10^{-13}	68
4c	130								0.177		0.074	7.15×10^{-13}	62
5a	150	364	760	2275	none	106	337	2.8	0.298	0.0083	0.021	1.97×10^{-11}	69
5b	600	361	760	2570	10 ⁶	C ₂ H ₅ Cl	331	2.7	0.599	0.0080	0.008	3.85×10^{-11}	0
						C ₂ H ₆							
6a	40	535	760	2382	none	203	339	2.9	0.911	0.0086	0.105	2.66×10^{-14}	96
6b	80					CFCl ₂ H			0.825		0.104	2.91×10^{-14}	89
6c	810 ^f								0.977		0.104	3.14×10^{-14}	112
7a	70 ^f	654	760	2096	none	196	348	2.7	0.959	0.0088	0.163	3.9×10^{-15}	22 ^g
7b	190 ^f					134a			0.908		0.162	3.2×10^{-15}	11 ^g
8a	2580 ^h	654	760	0	none	no ref	341	3.0	1.002	0.0088	0.0133		0
9a	2940	740	760	0	none	no ref	351	2.9	1.010	0.0081	0.117		0
9b	19620 ^h	740	760						1.025		0.205		0
9c	67680 ^h	740							1.126		0.205		0
10a	33 ^h	849	720	0	none	no ref	27	668	1.02	25.2	0.624		0
10b	600 ^h								0.96 ⁱ		0.260		0
10c	1500 ^h								0.93 ⁱ		0.261		0

^a t_{irr} (s) = irradiation time in seconds. $(Z + E)_i/(Z + E)_0$ [or $\text{ref}_i/\text{ref}_0$] = fraction of the sum of the Z- and E-CF₃CH=CHCF₃ isomers (or reference compound) remaining after irradiation. Data labeled a, b, c have the same initial concentrations and differ in t_{irr} only. ^bInitial reactant mole fractions in ppm; O₂ = "none" means no O₂ is added to the mix but an O₂ contaminant may be present. ^cRatio of E and Z isomers after irradiation or thermal reaction. A constant value with increasing time represents K_{eq} . ^dEffective rate constant of the Cl + CF₃CH=CHCF₃ reaction (cm³ molecule⁻¹ s⁻¹); for definition, see section 3.2.1. ^eMolar yield (%) of RCl₂=CF₃CFClCHCl. ^fNo irradiation. Time represents residence time in the reactor. Cl is generated by thermal dissociation of Cl₂. ^gLow apparent yield at this temperature is likely caused by secondary consumption. See discussion in text. ^hThermal isomerization only. No Cl catalysis can occur because no Cl₂ is present in the initial mixture. ⁱMeasurable pentafluoropropene was lost at this temperature as verified by appearance of a 4–7% yield of an unidentified product.

Table 2 presents selected data used to determine the rate constant k_4 for the reaction $\text{Cl} + \text{CF}_3\text{CF}=\text{CHF}$ by the relative rate method under varying conditions as defined in the table. The identities of the reference compounds are presented in the table under their initial mole fractions. Most of the data is obtained starting with the *Z* isomer, but at 297 and 454 K experiments were also performed beginning with the *E* isomer (data sets 2 and 4, respectively). In the absence of O_2 , reactions $-4a$ and $-4b$ compete only with reaction 5, which forms the dichloride, by a relatively slow reaction. The rate constants of reactions $-4a$ and $-4b$ will increase rapidly as the temperature increases because, based on the *ab initio* calculations of Papadimitriou et al. discussed above, they have activation energies of $\sim 17 \text{ kcal mol}^{-1}$. This will lower the steady state concentration of the alkyl radicals formed by Cl addition as the temperature rises. Because the relative rate method can only measure the net rate of removal of the $\text{CF}_3\text{CF}=\text{CHF}$ relative to a reference compound [e.g., for reaction 4, $(\ln C/C_0)/(\ln C/C_0)_{\text{ref}} = k_4/k_{\text{ref}}$], this will reduce the measured net rate of removal of the $\text{CF}_3\text{CF}=\text{CHF}$ to form the dichloride. One key point in the relative rate measurements is that the net consumption of $\text{CF}_3\text{CF}=\text{CHF}$ by Cl is occurring in parallel with the isomerization at temperatures above ambient. For this reason, neither k_{4a} nor k_{4b} can be determined individually from the fractional loss of one isomer alone simply by starting with that isomer in the initial mixture. This rate constant is determined instead from the fractional loss of the sum of the two isomers as shown in the Table 2 $[(Z + E)_t/(Z + E)_0]$. This makes the reasonable assumption that the *Z* and *E* isomers react with Cl at the same rate, an assumption that will be investigated below.

The net rate of removal of $\text{CF}_3\text{CF}=\text{CHF}$ in N_2 is defined herein as the effective rate constant $k_4(\text{eff})$, which includes both k_4 and the retarding effect of k_{-4} for the specific initial condition under study. Figure 4 presents a plot of $k_4(\text{eff})$ vs $1/T$. The experimental data points in N_2 diluent are shown as the open circles and triangles in the figure. In N_2 diluent, the effective rate constant decreases by a factor of 10^4 over the temperature range 297 to 665 K, because reaction -4 becomes

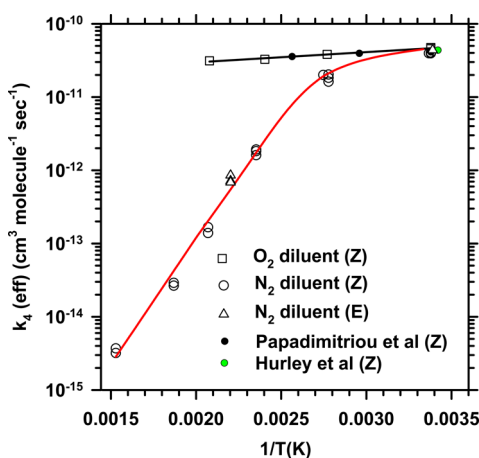


Figure 4. Plot of $k_4(\text{eff})$ for the reaction $\text{Cl} + \text{CF}_3\text{CF}=\text{CHF}$ as a function of $1/T(\text{K})$. Results are shown in two diluents: 760 Torr of N_2 (red line, \circ and \triangle); 760 Torr O_2 (black line, \square). Also shown are temperature-dependent data obtained by Papadimitriou et al.²¹ in 630 Torr of air diluent (black \circ), and experiments by Hurley et al.²² in 700 Torr of air at 0.296 K (green \bullet). $k_4 = 1.56 (\pm 0.22) \times 10^{-11} \text{ e}^{+643/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is obtained from the data in O_2 (see text).

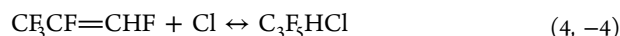
much faster as the temperature increases slowing the net loss rate of $\text{CF}_3\text{CF}=\text{CHF}$. At temperatures above 665 K, it was no longer possible to measure $k_4(\text{eff})$ because the reaction becomes very slow and no suitable reference species having a sufficiently slow rate constant was available.

When pure O_2 is the diluent, the addition rate constant decreases very slowly with increasing temperature over the range 297–483 K as shown in Figure 4. This occurs because O_2 traps the chloropentafluoropropenyl radicals via reaction 6, thereby preventing the loss of Cl to reform $\text{CF}_3\text{CF}=\text{CHF}$ by reaction $-4a$ or $-4b$. The rate constant in the presence of pure O_2 represents the true value of k_4 since the reverse reaction is completely suppressed throughout the temperature range as discussed in more detail previously for $\text{CF}_3\text{CF}=\text{CH}_2$.²⁰ The temperature-dependent rate constants in oxygen are fitted well by the Arrhenius expression, $k_4 = 1.56 (\pm 0.22) \times 10^{-11} \text{ e}^{+643(\pm 190)/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in which the error limits are 2σ . This is an overall rate constant encompassing the formation of both of the chloropentafluoropropenyl radicals resulting from reactions 4a and 4b. Not enough product information is available in these experiments to determine k_{4a} and k_{4b} individually. As shown in Figure 4, this rate constant expression for k_4 agrees with the measurements of k_4 by Papadimitriou et al.²¹ (Table 2 of that reference) in approximately 630 Torr of zero air diluent at 296, 338, and 380 K. It also agrees with the data of Hurley et al. in 700 Torr of air at 296 K.²²

The value of k_4 for the *E* isomer (data points 2a–2d) is indistinguishable from that of the *Z* isomer (1a–1f) at 297 K verifying the assumption made in the preceding paragraph that the rate constants for the *Z* and *E* isomers are identical. Note that the ratio E_t/Z_t remains >18 for all values of t_{irr} in the 2a–2d data set, showing that the *E* isomer is dominant throughout. Therefore, at 297 K, $k_4(\text{eff})$ for the *E* isomer is actually being measured and is indistinguishable from that of the *Z* isomer (see 1a–1f where the *Z* isomer is dominant throughout). The 2a–2d data set does show that catalysis is occurring at ambient temperature because the E_t/Z_t ratio is decreasing toward equilibrium. However, the catalysis is very slow because the reverse reaction (k_{-4}), which is necessary for catalysis to occur, is slow at ambient temperature. Only at elevated temperature does the reverse reaction become sufficiently fast to produce rapid catalysis of the isomerization as shown by points 4a–4c at 454 K. At 454 K, the *E* to *Z* isomerization is almost equilibrated at 40 s (see E_t/Z_t for data points 4a–4c), which is the minimum time for filling, irradiating, and sampling the high-temperature reactor. This experiment, even though it starts with the *E* isomer, actually is measuring $k_4(\text{eff})$ for the *Z* isomer because of the rapid isomerization that occurs. Therefore, there is no way to measure $k_4(\text{eff})$ for the *E* isomer at this temperature in these experiments. The series of data (4a–4c) in Table 2 illustrates another important point regarding the use of Cl atoms as a catalyst for the isomerization reaction. Even though the fraction of $\text{CF}_3\text{CF}=\text{CHF}$ remaining after the irradiation $([E + Z]_t/[E + Z]_0)$ decreases from 0.616 to 0.177 as the irradiation time increases, the value of (E_t/Z_t) reaches a constant value (data 4b and 4c) equal to 0.074, which represents the equilibrium constant K_1 of the *Z* to *E* isomerization. This demonstrates that the parallel reactions 5a and 5b of the chlorofluoroalkyl radical adduct with Cl_2 to form the dichloride do not affect the measurement of K_1 in these experiments.

A simplified modeling study of the addition–decomposition process (reactions 4, -4), similar to that for $\text{CF}_3\text{CF}=\text{CH}_2$,²⁰

was performed in order to estimate the exothermicity of reaction 4. This estimation was carried out using a computer model of reactions 4 and 5 in a simplified form plus a reference species (RH) to mimic the relative rate measurements. The kinetics solver Acuchem¹⁸ introduced in section 3.1 was used again to perform these calculations. This model assumes that the only reactions occurring in the mixture are



The value of k_4 which represents the rate constant in the absence of reverse reaction is determined from an Arrhenius fit to the data in Figure 4 in the presence of 100% O₂ from 297 to 483 K. The high O₂ mole fraction scavenges the chlorofluoroalkyl radicals formed in reaction 4 suppressing the reverse reactions, giving $k_4 = 1.56 (\pm 0.22) \times 10^{-11} \text{ e}^{+643(\pm 190)/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as described above. The rate constant for the reference reaction 9 in the model is chosen to be compatible with the $k_4(\text{eff})$ presented in Figure 4 at a chosen temperature. Reaction 10 forms an alkyl chloride from the radical formed from the reference reaction 9. The value of k_5 was not measured in our experiments. As an approximation, we used the expression for the similar reaction $\text{CF}_3\text{CFCH}_2\text{Cl}$ or $\text{CF}_3\text{CFClCH}_2 + \text{Cl}_2 \rightarrow \text{CF}_3\text{CFClCH}_2\text{Cl} + \text{Cl}$, which was determined in ref 20 for the $\text{CF}_3\text{CF}=\text{CH}_2$ system [$k = 1.2 \times 10^{-12} \text{ e}^{-3000/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$]. The decomposition rate constant (k_{-4}) was then fitted to the temperature-dependent $k_4(\text{eff})$ data in Figure 4 in the absence of O₂. The value of $k_4(\text{eff})$ from the model was calculated exactly as in the relative rate experiment {i.e., $k_4(\text{eff})/k(\text{ref}) = \ln[(\text{CF}_3\text{CF}=\text{CHF})_t/(\text{CF}_3\text{CF}=\text{CHF})_0]/\ln[(\text{ref})_t/(\text{ref})_0]}$. The expression for this rate constant derived as described is $k_{-4} = 1.12 \times 10^{13} \text{ e}^{-16865/RT} \text{ s}^{-1}$. The best fit to the data in the absence of O₂ using this value of k_{-4} is represented by the red line through the oxygen-free data in Figure 4. The activation energy of k_{-4} agrees with the exothermicity of the two radicals formed in reaction 4 calculated by Papadimitriou et al. (16.1 and 17.9 kcal mol⁻¹).²¹

Because an approximate estimate of k_5 has been used in the model, two additional calculations were carried out to estimate the effect of uncertainty in k_5 on the temperature dependence of k_{-4} . First, increasing (or decreasing) the A factor of k_5 by a factor of 10 caused a corresponding factor of 10 increase (or decrease) in the A factor of k_{-4} required to achieve a fit equivalent to the red line in Figure 4. The increase (or decrease) in A factor did not affect the calculated activation energy of k_{-4} . Second, if the activation energy of k_5 is reduced to zero (e.g., decreased by 3 kcal mol⁻¹), the activation energy of k_{-4} must be decreased by 3 kcal mol⁻¹ to achieve a fit of a quality similar to the red line in Figure 4. Similarly, raising the activation energy by 3 kcal mol⁻¹ requires a 3 kcal mol⁻¹ increase in the activation energy of k_{-4} . The exothermicity of reaction 4 is $17 \pm 3 \text{ kcal mol}^{-1}$ on the basis of this estimation of the activation energy of k_{-4} and an estimate of the uncertainty.

3.2.2. Enthalpy of Isomerization of CF₃CF=CHF. The enthalpy of the Z to E isomerization of CF₃CF=CHF was determined from the temperature dependence of the equilibrium constant (K_1) using thermal isomerization without the presence of Cl₂ at temperatures above 654 K combined with Cl atom catalyzed isomerization at lower temperatures.

Selected data used in these measurements are presented in Table 2. The equilibrium constant at a given temperature was determined from the ratio of the two isomers (E_t/Z_t) as a function of either irradiation time if Cl catalyzed or time in the reactor if not. When the ratio remains constant for two significantly different exposure times, this value was defined as K_1 at that temperature. One other condition also must be satisfied. The final ratio (E_t/Z_t) of the isomers must be different from that in the initial mixture; otherwise, it cannot be determined whether the initial mixture was at equilibrium or the isomerization was too slow to be observed.

These points are illustrated in Table 2. At 297 K, experiments 1a–1f for the Z to E isomerization show no significant change in the E_t/Z_t ratio from that of E_0/Z_0 as the irradiation time increases, and no determination of the equilibrium constant is possible. Experiments 2a–2d show measurements at 297 K starting from the E isomer. In this case, E_t/Z_t does change with irradiation time, but the ratio does not reach a constant value, and again no determination of K_1 can be obtained from these data.

The Cl catalyzed data (4a–4c) at 454 K present a successful determination of K_1 starting from the E isomer. The initial value E_0/Z_0 is 25.8. After 40 s of irradiation $E_t/Z_t = 0.068$, and the ratio does not change significantly with longer irradiation times. Thus, it is at equilibrium, and $E_t/Z_t [\text{av}] = 0.072 = K_1$ at 454 K.

Data points 5a and 5b, while not identical mixtures, are similar except that 5a has N₂ as diluent and 5b is in O₂. These points illustrate the effect of adding pure O₂ as the diluent for a catalyzed Z to E isomerization. $k_4(\text{eff})$ measured in N₂ (data point 5a) is a factor of 2 slower than k_4 measured in O₂ (data point 5b) near 362 K. In O₂, the rate of isomerization slows dramatically as can be seen by comparing 5b to 5a. In N₂ (5a), the isomerization is nearing equilibrium after 40 s of irradiation at 364 K ($E_t/Z_t = 0.021$, $K_1 = 0.0227$, see Figure 5), while at 361 K in O₂, no measurable isomerization has taken place after 600 s. The ratio $E_t/Z_t = 0.008$ for data point 5b is identical to

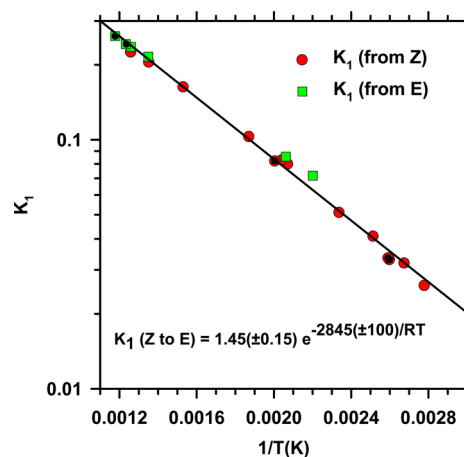


Figure 5. Equilibrium constants (K_1) for the isomerization reaction $\text{Z-CF}_3\text{CF}=\text{CHF} \rightarrow \text{E-CF}_3\text{CF}=\text{CHF}$ plotted as a function of $1/T$. Selected individual data points in this figure are tabulated in Table 2. Data are shown starting from both E and Z isomers. The temperature-dependent expression for K_1 is presented in the figure. Conditions: 740 K to maximum = thermal only, no Cl₂; 654 K = Cl₂ with no irradiation; 535 K and below = Cl₂ with irradiation. Red and green symbols with black dot in center = GasPro GC column; symbols without black dot = DB1 GC column (see Experiments section).

Table 3. Results and Initial Conditions for Selected E to Z (and one Z to E) Thermal Isomerization of CF₃CF=CHF Whose Rate Constants Are Plotted in Figure 6

E to Z Isomerization ^c											
data	<i>t</i> ^a (s)	T (K)	P (Torr)	Z ₀ ^b (ppm)	E ₀ ^b (ppm)	Z _{<i>t</i>} ^b (ppm)	E _{<i>t</i>} ^b (ppm)	[(Z + E) _{<i>t</i>}]/[(Z + E) ₀] ^c	K ₋₁ ^d calcd	E _{eq} ^d (ppm)	k ₋₁ ^f (s ⁻¹)
1a	5340	704	760	27	667	120	574	0.999	5.277	110	2.92 × 10 ⁻⁵
1b	23 070	701	750			280	417	1.005	5.323	110	2.17 × 10 ⁻⁵
2a	1200	727	760	27	644	86.8	583	1.020	4.948	113	8.47 × 10 ⁻⁵
2b	4920	727	820			245	424	1.015	4.948	113	9.05 × 10 ⁻⁵
2a	374	760	770	25	630	138	517	0.998	4.542	118	5.49 × 10 ⁻⁴
2b	730	760	760			221	434	1.007	4.542	118	5.41 × 10 ⁻⁴
2c	1710	761	700			392	263	1.004	4.531	118	6.06 × 10 ⁻⁴
3a	228	766	800	24	612	121	515	1.021	4.50	116	7.83 × 10 ⁻⁴
3b	772	766	770			305	331	1.000	4.50	116	8.89 × 10 ⁻⁴
3c	1830	765	725			436	200	1.013	4.50	116	7.92 × 10 ⁻⁴
4a	73	814	805	17	422	182	257	1.020	4.005	87.7	7.46 × 10 ⁻³
4b	50	814	111			126	313	1.016	4.005	87.7	6.34 × 10 ⁻³
4c	85	814	89			180	259	1.040	4.005	87.7	6.31 × 10 ⁻³
4d	134	814	100			237	202	1.008	4.005	87.7	6.41 × 10 ⁻³
5a	31	849	600	27	668	417	278	1.018	3.728	147	3.53 × 10 ⁻²
5b	33	849	720			428	267	1.018	3.728	147	3.51 × 10 ⁻²
5c	65	848	760			517	178	1.013	3.735	147	3.43 × 10 ⁻²
5d	36	849	100			421	274	1.019	3.728	147	3.09 × 10 ⁻²
Z to E Isomerization ^c											
data	<i>t</i> ^a (s)	T (K)	P (Torr)	Z ₀ ^b (ppm)	E ₀ ^b (ppm)	Z _{<i>t</i>} ^b (ppm)	E _{<i>t</i>} ^b (ppm)	[(Z + E) _{<i>t</i>}]/[(Z + E) ₀] ^c	K ₁ ^d calcd	Z _{eq} ^d (ppm)	k ₁ (s ⁻¹)
4a	57	793	760	674	6	646	34	0.997	0.238	549	8.50 × 10 ⁻⁴
4b	82	793	760			641	39	0.970	0.238	549	7.08 × 10 ⁻⁴
4c	160	793	760			601	79	0.998	0.238	549	1.05 × 10 ⁻³

^aTime in reactor. ^bInitial and final reactant mole fractions. ^cTotal pentafluoropropene fractional recovery. ^dEquilibrium constant at the stated temperature calculated from the data in Figure 5. $E_{eq} = (Z_0 + E_0)/(1 + K_{-1})$; $Z_{eq} = (Z_0 + E_0)/(1 + K_1)$. ^eRate constant data includes starting from the *E* or *Z* isomers as indicated. ^fRate constant for reaction 1, −1. These are the values used in generating Figure 6. Values calculated using the mole fractions in the table may deviate slightly because of round off.

the starting ratio in the unreacted mixture. This illustrates clearly the catalytic mechanism of the Cl atom discussed above in the absence of O₂. In N₂, the instability of the C₃F₅HCl adduct with respect to dissociation back to reactants at even moderately elevated temperature results in multiple passes through the reversible system represented by reaction 4, −4. This allows reaction 1 to equilibrate. When ~760 Torr of O₂ is added, the majority of the C₃F₅HCl adduct radicals are trapped irreversibly as stable peroxy radicals. Reaction −4 cannot occur, thereby stopping the catalyzed isomerization of reaction 1 at this temperature.

Data set 6 presents experiments in N₂ diluent at 535 K in the presence of Cl₂ both with (6a and 6b) and without (6c) irradiation of the mixture. Both cases produce isomerization to equilibrium indicating that, at this temperature, Cl₂ can be dissociated both by irradiation and by thermal dissociation.

The two data sets 7 and 8 at 654 K illustrate the effectiveness of the Cl catalysis process. Data set 7 contains Cl₂, but the reactor is not irradiated. The thermal dissociation of Cl₂ produces an equilibrium *E*_{*t*}/*Z*_{*t*} ratio after 70 s. No change in the ratio occurs with additional time in the reactor, verifying that the isomers are equilibrated. Data point 8a contains no Cl₂, and thermal isomerization is barely visible after 2580 s as shown by the slight increase in the value of *E*_{*t*}/*Z*_{*t*} (=0.0133) relative to *E*₀/*Z*₀ (=0.0088). Above ~700 K, the equilibrium constant is determined thermally without Cl catalysis because it has become sufficiently fast.

The measured values of *K*₁(*T*) for the *Z* to *E* isomerization are plotted versus *T*^{−1} in Figure 5. There is no curvature evident within experimental error in the plot of *K*₁ versus 1/*T*

over the temperature range studied (365–850 K). The linear least-squares expression fitted to the equilibrium constants is represented by $K_1 = 1.45(\pm 0.15)e^{-2845(\pm 100)/RT}$, in which the error limits are 2σ. The enthalpy of isomerization Δ*H*₁ = +2.843(±0.1) kcal mol^{−1} and the entropy of isomerization Δ*S*₁ = *R* ln(1.45) = 0.74 eu are obtained from the equation for *K*₁. The measured enthalpy of isomerization and its positive sign indicates that the *Z* configuration (with the fluorine atoms cis to one another across the double bond) is lower in energy than the *E*(trans) configuration. Therefore, CF₃CF=CHF shows a fluorine “cis effect” similar to that discussed in the Introduction for 1,2-difluoroethylene.

However, the cis difluoroethylene lies 930 cal mol^{−1} lower in energy than the trans isomer. Thus, the effect is substantially larger in the case of *Z*-CF₃CF=CHF.

3.2.3. Isomerization Rate Constant of CF₃CF=CHF. Table 3 presents selected data points measuring the *E* to *Z* (and one *Z* to *E*) isomerization rate constants of CF₃CF=CHF for the temperature and pressure ranges studied. This high-temperature isomerization exhibited no significant parallel decomposition channel in contrast to the 2-butene experiments as shown by the fact that the fractional recovery $\{(Z + E)_t/(Z + E)_0\}$ equals 1 at all temperatures to within experimental error. Equations A–C, which are used to obtain the rate constants from the experimental data, were discussed during the 2-butene analysis in section 3.1. Figure 6 presents a plot of *k*_{−1} (*E* to *Z* isomerization) as a function of the reciprocal of the temperature. The pure *E* isomer was chosen as the initial species for all but one of the data sets because it is the least stable isomer and is farther from its equilibrium mole fraction

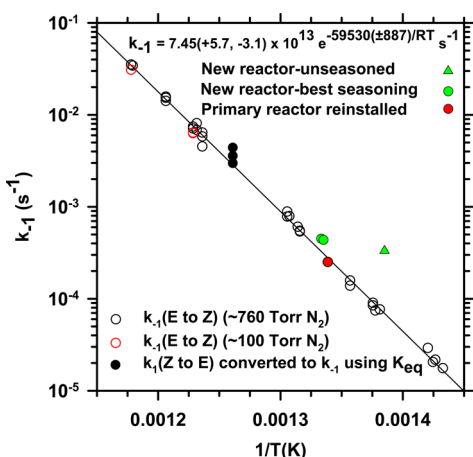


Figure 6. Plot of the rate constant (k_{-1}) of the isomerization reaction $E\text{-CF}_3\text{CF=CHF} \rightarrow Z\text{-CF}_3\text{CF=CHF}$ in 760 Torr of N_2 as a function of $1/T$. No Cl_2 is present in any of these experiments. Detailed initial conditions and results are presented in Table 3 for selected data points in this figure. The data points in this figure are discussed in detail in section 3.2.3. The rate constant expression derived from the data is included in this figure. Error limits are 2σ . The data points at 747 K (red filled circle) and 737 K (black open circles) were obtained using the DB1 GC Column. All other data were measured using the GasPro column (see Experiments section). The effect of reactor seasoning is described in section 3.2.3.

than is the pure Z isomer, providing greater measurement accuracy. The rate constant k_1 obtained from the data set starting from the Z isomer was converted to k_{-1} using the equilibrium constant expression presented above before its inclusion in Figure 6. The high-pressure data for k_{-1} were fitted to an Arrhenius expression using a linear least-squares regression yielding $k_{-1} = 7.45(+5.7, -3.1) \times 10^{13} e^{-59530/(887)/RT} \text{ s}^{-1}$ for the E to Z isomerization rate constant. The low-pressure data points near 100 Torr shown in Figure 6 (red open circles) are indistinguishable from those at 760 Torr verifying that k_{-1} is at the high-pressure limit.

An additional test was performed to verify that surface reactions were not a major source of error. The primary reactor in which all previous reactions were performed had been in use for several years for measurements of Cl atom reactions. A different reactor of the same dimensions, but used very little in previous Cl studies, was installed in the oven. The first measurement of k_{-1} in this reactor yielded the rate constant shown by the green filled triangle at ~ 720 K, which is approximately four times greater than the value of the rate constant measured in the primary reactor at that temperature. After placing a mixture in the new reactor and letting it react for ~ 18 h, the measured value decreased to very near the primary reactor line as shown by the green filled circles at ~ 745 K. It is likely that with additional seasoning the measurement would approach closer still to that of the primary reactor, but even without more seasoning, the result agrees with the primary reactor data to within the data scatter. When the primary reactor was reinstalled, the agreement with the previous data in that reactor was excellent (red filled circle). On the basis of this test, the data are free from measurable surface reaction effects. In these E isomer experiments there is a slight (4%) Z isomer contamination in the initial mixture, which does not affect the rate constant calculation within experimental error.

3.3. Isomerization of $Z\text{-CF}_3\text{CH=CHCF}_3$. 3.3.1. Rate Constant of the Cl Addition Reaction. Table 4 contains

selected data sets (both Cl catalyzed and purely thermal) for determining equilibrium constants and Cl addition rate constants for $\text{CF}_3\text{CH=CHCF}_3$. All but one of the data sets start from the $Z(\text{cis})$ isomer. These data are similar to those described for $\text{CF}_3\text{CF=CHF}$ and will not be discussed in as much detail. The last column contains the reaction rate constants $k_7(\text{eff})$ for the Cl addition to the double bond of $\text{CF}_3\text{CH=CHCF}_3$ over the temperature range 297–383 K. Higher temperatures could not be explored because $k_7(\text{eff})$ is much slower than $k_4(\text{eff})$ in N_2 , and at higher temperatures no suitable reference compound with a comparably slow rate constant was available. All of the experiments in Table 4 started with $Z\text{-CF}_3\text{CH=CHCF}_3$ as the initial reactant. However, in N_2 diluent, the Z isomer is quickly converted to the E isomer (note that $E_i/Z_i > 1$ for most of the data points 1–8 in Table 4) and the Cl addition reaction must proceed mainly via the E isomer. This indicates that $k_7(\text{eff})$ is actually being measured for the E isomer. As shown previously for $\text{CF}_3\text{CF=CHF}$, it is reasonable to assume that k_7 for the E isomer is very similar to k_7 for the Z isomer.

Figure 7 presents plots of $k_7(\text{eff})$ versus $1/T$ in N_2 , O_2 , and N_2/O_2 diluents. Experiments in N_2 are denoted by square symbols. Those in pure O_2 are shown as circles, and those in a 100 Torr O_2 /660 Torr N_2 mix appear as triangles. The rate expression in pure O_2 can be represented by $k_7 = 1.05 \times 10^{-12} e^{+1874/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This represents the true rate constant of the addition of Cl to the double bond, k_7 , in $Z(\text{or } E)\text{-CF}_3\text{CH=CHCF}_3$ as discussed in section 3.2.1 for $\text{CF}_3\text{CF=CHF}$. It is not $k_7(\text{eff})$ because 760 Torr of O_2 has totally suppressed the reverse reaction, k_{-7} , to within experimental error. Verification of this total suppression was obtained by reducing the O_2 partial pressure to 100 Torr, and noting that the rate constant remained the same at both O_2 partial pressures to within experimental error. This confirms that the reverse reaction is totally suppressed at O_2 partial pressure above 100 Torr.

Although k_7 has a very similar value to k_4 in O_2 , in N_2 diluent, $k_7(\text{eff})$ is orders of magnitude smaller than $k_4(\text{eff})$ at the same temperature ($k_7 \sim 5 \times 10^{-15}$ and $k_4 \sim 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at ~ 380 K in Figures 4 and 7, respectively). The data in N_2 diluent in Figure 7 were fitted to a chemical mechanism exactly analogous to reactions 4, 5, 9, and 10 described in section 3.2.1 for $\text{CF}_3\text{CF=CHF}$. The initial rate constant assumptions were similar to those for $\text{CF}_3\text{CF=CHF}$: $k_7 = 1.05 \times 10^{-12} e^{+1874/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and $k_8 = 1.2 \times 10^{-12} e^{-3000/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The best fit to the N_2 data in Figure 7 results in the expression $k_{-7} = 9.7 \times 10^{15} e^{-16500/RT} \text{ s}^{-1}$ (red line in Figure 7). This expression has a large A factor for a first order reaction. Analogous to the discussion of the fits to the $\text{CF}_3\text{CF=CHF}$ data in section 3.2.1, reducing the A factor of reaction 8 by 2 orders of magnitude gives the same fit provided that the A factor of k_{-7} is reduced by the same factor with no change of the activation energy. It seems likely that the rate constant k_8 is smaller than that of k_5 , the $\text{CF}_3\text{CF=CHF}$ analogue, causing $k_7(\text{eff})$ to be smaller than $k_4(\text{eff})$ as noted above, although this cannot be proven from the data. Also analogous to the discussion of the $\text{CF}_3\text{CF=CHF}$ fits, increasing or decreasing the activation energy of k_8 by 3 kcal mol^{-1} increases or decreases the E_a of k_{-7} by the same amount to achieve a similar quality of fit to the data. Therefore, we believe a reasonable estimate of the exothermicity of reaction 7 is equal to the activation energy of k_{-7} or $16.5 \pm 3 \text{ kcal mol}^{-1}$ on the basis of the discussion of $\text{CF}_3\text{CF=CHF}$ in section 3.2.1.

Table 4. Results and Initial Conditions for Selected Experiments (Data at 300 K Are in the 500 cm³ Reactor) on the Enthalpy of Isomerization of Z-CF₃CH=CHCF₃ Presented in Figure 8 and Its Reaction Rate Constants with Cl Presented in Figure 7

data	t_{irr}^a (s)	T (K)	P (Torr)	Cl ₂ ^b (ppm)	O ₂ ^b (ppm)	ref ₀ ^b (ppm)	Z ₀ ^b (ppm)	E ₀ ^b (ppm)	$[(Z + E)_t]/[(Z + E)_0]^a$	$(\text{ref})_t/(\text{ref})_0^a$	E ₀ /Z ₀	E _t /Z _t ^c	k_7 (eff) ^d
1a	60	297	980	1605	none	125	302	2.8	0.887	0.282	0.0093	35	7.77×10^{-13}
1b	120	297	980			C ₂ H ₅ Cl			0.802	~0.02		~4500 ^e	
2	68	297	680	1824	none	83	397	4.2	0.896	0.984	0.014	35.1	7.15×10^{-13}
						CH ₄							
3a	60	297	980	1814	none	108	390	2.0	0.905	0.05	0.005	1.24	1.97×10^{-12}
3b	150	297	980			C ₂ H ₆			0.796	<0.001		~4500 ^e	
3c	330	297	980						0.591	<0.001		~4100 ^e	
4a	330	344	760	1847	none	83	337	2.6	0.859	0.333	0.008	1020	2.80×10^{-14}
4b	780	342	760			CH ₄			0.765	0.060		934	1.93×10^{-14}
5a	300	383	750	1762	none	78	342	4.0	0.939	0.461	0.012	532	5.10×10^{-15}
5b	720	382	750			CFCl ₂ H			0.882	0.074		525	3.00×10^{-15}
6a	10	453	750	1900	none	no ref	230	8.5	0.996		0.035	235	
6b	60	453	760						0.993			271	
6c	180	453	780						0.978			234	
6d	70n.i. ^f	453	700						0.995			0.554	
6e	35	559	650						0.991			94.4	
6f	99n.i. ^f	560	600						0.993			26.5	
7a	310n.i. ^f	548	780	1914	none	no ref	359	6	0.999		0.017	96	
7b	902n.i. ^f	548	770						0.999			108	
7c	7800n.i. ^f	545	750						0.999			111	
8a	34	852	810	0	none	no ref	445	1	0.996		0.002	25	
8b	1500	852	750						1.024			22.6	
9a	30	297	740	1803	~10 ⁶	100	343	1	0.971	0.937	0.002	0.004 ^g	2.66×10^{-11}
9b	90	297	740			C ₂ H ₆			0.914	0.807		0.010	2.48×10^{-11}
9c	390	297	740						0.610	0.305		0.047	2.45×10^{-11}
9d	445	376	760						0.922	0.672		0.039	1.28×10^{-11}
9e	840	376	760						0.852	0.465		0.077	1.31×10^{-11}
9f	1260	376	740						0.777	0.306		0.119	1.28×10^{-11}

^a t_{irr} (s) = irradiation time in seconds. $(Z + E)_t/(Z + E)_0$ [or $\text{ref}_t/\text{ref}_0$] = the fraction of the sum of the Z- and E-CF₃CH=CHCF₃ isomers (or reference compound) remaining after irradiation. Data labeled a, b, and c have the same initial concentrations and differ in t_{irr} only. ^bInitial reactant mole fractions in ppm; O₂ = "none" means no O₂ is added to the mix but an O₂ contaminant may be present. ^cRatio of E and Z isomers after irradiation or thermal reaction. A constant value with increasing reaction time represents K_{eq} . ^dEffective rate constant of the Cl + CF₃CH=CHCF₃ reaction (cm³ molecule⁻¹ s⁻¹). For definition see section 3.2.1. ^eEstimated error is 30% because of the very small Z isomer mole fraction, not included in the fit to data in Figure 8. ^fNotation n.i. = no irradiation present, indicating thermal decomposition of Cl₂ or a purely thermal isomerization in the absence of Cl₂. ^gIsomerization suppressed in this series by the presence of O₂ even though $k(\text{eff})$ is very fast (see discussion in text).

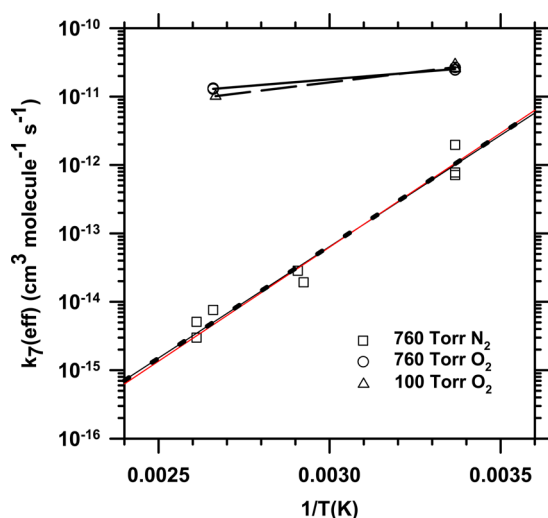


Figure 7. Plot of $k_7(\text{eff})$ for the reaction Cl + CF₃CH=CHCF₃ in N₂ diluent as a function of $1/T$ (□). The true value of k_7 with k_7 suppressed is obtained from the data in O₂ diluent (see text).

3.3.2. Enthalpy of Isomerization of CF₃CH=CHCF₃. The enthalpy of the Z to E isomerization of reaction 2 was determined from measured equilibrium constants (K_2) over the temperature range 297–850 K. Selected measurements of the equilibrium constants are presented in Table 4, covering the entire temperature range. In the absence of Cl₂, there is no evidence of a parallel decomposition reaction at high temperature that was observed with 2-butene, and no correction is needed (see data 8a and 8b). All measurements of the Z to E equilibrium constant, K_2 , are plotted in Figure 8 as a function of $1/T$. All but one of the measurements were obtained from starting mixtures containing the Z isomer. At the highest temperature, one data point (red filled circle) was determined starting with the E isomer. At this temperature, the equilibrium constant was independent of the identity of the isomer in the mixture as required by thermodynamics.

All points in Figure 8 except that at ambient temperature were fitted by a linear least-squares algorithm giving $K_2 = 1.9(\pm 0.22)e^{+4330(\pm 120)/RT}$. The error limits represent 2σ as for all error limits herein. The point at 297 K in this figure was not included in the fit because the equilibrium mole fraction of the Z isomer was so small that uncertainty in GC measurement caused an uncertainty of ~30% in this point. However, it is

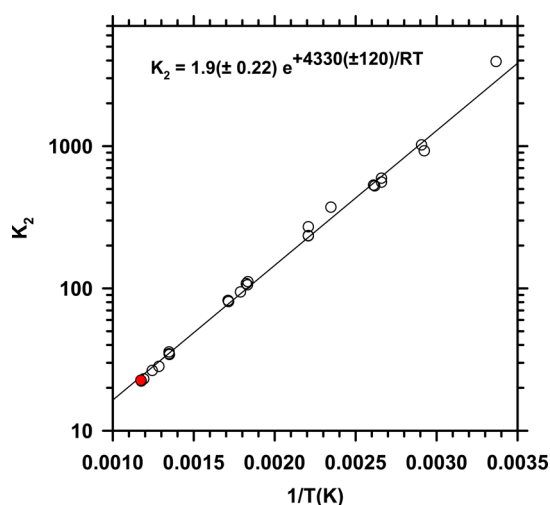


Figure 8. Equilibrium constants (K_2) for the isomerization reaction $Z\text{-CF}_3\text{CH=CHCF}_3 \rightarrow E\text{-CF}_3\text{CH=CHCF}_3$ plotted as a function of $1/T$. Selected individual data points in this figure are tabulated in Table 4. The temperature-dependent expression for K_2 fitted to the data is presented in the figure. All data points were obtained starting with the *Z* isomer except the red filled circle. That point was obtained starting with the *E* isomer.

consistent with the more precise higher temperature data used in the fit. There might be slight curvature in the plot, but within experimental error, it is linear over the temperature range used in the K_2 fit (340–850 K). On the basis of the expression for the *Z* to *E* equilibrium constant, K_2 , the *Z* to *E* enthalpy of isomerization $\Delta H_2 = -4.33 \pm 0.12 \text{ kcal mol}^{-1}$ with the *Z*(cis) isomer higher in energy than that of the *E*(trans) isomer. The expression for K_2 also provides a measurement of the *Z* to *E* entropy of isomerization, $\Delta S_2 = R(\ln(1.9)) = +1.27(\pm 0.22) \text{ eu}$. The *E*(trans) isomer is lower in energy because of the

destabilizing steric interaction between the large CF_3 groups in the *Z*(cis) isomer precisely as is observed for *cis*-2-butene, and there are no F atoms present on the double bond carbon atoms to provide a stabilizing “cis effect.” Because CF_3 has a significantly larger van der Waals radius than CH_3 ,²³ the enthalpy of isomerization of reaction 2, ΔH_2 , is approximately ~4–6 times larger than that of 2-butene depending upon the temperature region being compared.¹⁷ The implications of these results with regard to the “cis effect” of octafluoro-2-butene will be discussed in section 4.1.2.

3.3.3. Isomerization Rate Constant of $Z\text{-CF}_3\text{CH=CHCF}_3$ (k_2). Table 5 presents all of the data obtained during measurements of the *Z* to *E* isomerization rate constant of $\text{CF}_3\text{CH=CHCF}_3$ over the temperature range 676–850 K. As mentioned earlier, there is no loss of this compound to parallel decomposition reactions such as was observed in 2-butene (see the fractional recovery $[(Z + E)_t]/[(Z + E)_0]$ column in Table 5), and no correction is required. Once again equations similar to A–C were used to calculate the rate constants from the experimental data. All but one of the rate constants were determined at pressures near 760 Torr. The pressure for data point 4d was 99 Torr to verify that the rate constants were at the high-pressure limit. Data points 4d and 4c were obtained from the same initial mixture at the same temperature and produce indistinguishable rate constants. Thus, at pressures above 100 Torr, this isomerization rate constant is at its high-pressure limit. Figure 9 presents a plot of the measured values of k_2 versus $1/T$, which yields the Arrhenius expression $k_2 = 7.78(+5.1, -3.3) \times 10^{13} \text{ e}^{-58845(\pm 675)/RT} \text{ s}^{-1}$.

4. DISCUSSION OF THE CURRENT MEASUREMENTS WHICH PERTAIN TO THE “CIS EFFECT”

4.1. Background. Table 6 summarizes current and past measurements of the *cis*/*trans* (or *trans*/*cis*) isomerizations of olefins whose kinetics and energetics have the possibility of

Table 5. Results and Initial Conditions for All *Z* to *E* Thermal Isomerizations Determining the Isomerization Rate Constants for $\text{CF}_3\text{CH=CHCF}_3$ in Figure 9

data	t^a (s)	T (K)	P (Torr)	Z_0^b (ppm)	E_0^b (ppm)	Z_t^b (ppm)	E_t^b (ppm)	$[(Z + E)_t]/[(Z + E)_0]^c$	K_2^d calcd	Z_{eq}^d (ppm)	k_2^e (s^{-1})
1a	3600	677	770	427	1	415	12	0.997	47.58	9	7.91×10^{-6}
1b	10 350	676	760			398	29	0.998	47.80	9	6.82×10^{-6}
1c	23 085	677	760			362	65	0.997	47.58	9	7.10×10^{-6}
2a	293	741	760	431	1	389	33	1.000	36.02	11.6	3.47×10^{-4}
2b	835	741	775			331	102	1.005	36.02	11.6	3.16×10^{-4}
2c	2155	740	775			212	223	1.008	36.17	11.6	3.34×10^{-4}
3a	200	774	750	401	1	274	130	1.006	31.78	12.3	1.91×10^{-3}
3b	629	774	780			133	270	1.005	31.78	12.3	1.80×10^{-3}
3c	73	774	760			344	58	0.990	31.78	12.3	2.10×10^{-3}
4a	208	800	740	356	1	94	265	1.007	29.00	11.9	6.67×10^{-3}
4b	84	799	790			206	152	1.005	29.10	11.9	6.58×10^{-3}
4c	50	808	600			234	124	1.002	28.22	12.2	8.47×10^{-3}
4d	195	808	99			76	283	1.007	28.22	12.2	8.32×10^{-3}
5a	43	837	730	346	1	78	271	1.002	25.71	13.0	3.70×10^{-2}
5b	88	837	690			28	315	0.998	25.71	13.0	3.37×10^{-2}
6a	42	850	900	445	1	57.4	292	1.006	24.70	17.3	5.42×10^{-2}
6b	80	850	840			23.5	426	1.006	24.70	17.3	5.10×10^{-2}
6c	35	851	760			72	375	1.005	24.63	17.3	5.64×10^{-2}

^aTime in reactor. ^bInitial (0) and final (t) reactant mole fractions. ^cRatio of total final to initial hexafluoro-2-butene mole fractions labeled fractional recovery in the text. ^dEquilibrium constant at the stated temperature calculated from the data in Figure 8. $Z_{\text{eq}} = (Z_0 + E_0)/(1 + K_2)$. ^eRate constant for reaction 2. These are the values used in generating Figure 9. Values calculated using the concentrations in the table may deviate slightly because of round off.

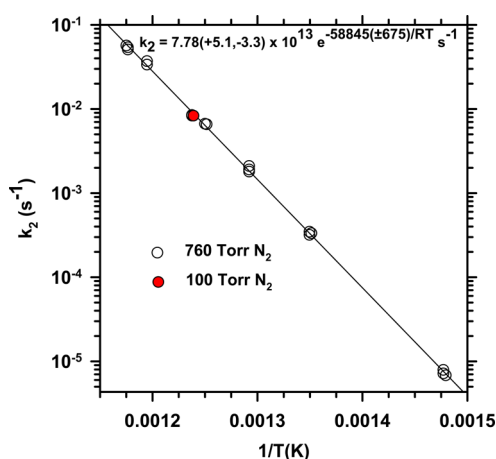


Figure 9. Plot of the rate constant (k_2) of the isomerization reaction $Z\text{-CF}_3\text{CH=CHCF}_3 \rightarrow E\text{-CF}_3\text{CH=CHCF}_3$ in 760 Torr of N_2 as a function of $1/T$. Detailed initial conditions and results are presented in Table 5 for the data points in this figure. The data points in this figure are discussed in detail in section 3.3.3. The rate constant expression derived from an Arrhenius fit to the data is included in this figure.

shedding additional light on the “cis effect” caused by fluorine substitution across the $\text{C}=\text{C}$ double bond. This table presents the enthalpy of isomerization, the entropy of isomerization, and the rate constant (A factor and activation energy) of isomerization for CHF=CHF , $\text{CF}_3\text{CF=CHF}$, $\text{CF}_3\text{CH=CHCF}_3$, $\text{CF}_3\text{CF=CFCF}_3$, and $\text{CH}_3\text{CH=CHCH}_3$. All measurements are absolute determinations except the measurements by Jeffers. Jeffers’ data were obtained in relative-rate shock tube experiments using either *cis*-2-butene isomerization or cyclohexene pyrolysis as reference. As described earlier, we have made adjustments where appropriate to Jeffers’ rate constants using the value for *cis*-2-butene determined in section 3.1 above and the slight adjustment to newest value of the rate constant for cyclohexene decomposition. When error limits are quoted in other publications at the 1σ level, they have been adjusted to 2σ in Table 6.

Prior to the measurements presented here, there were four experiments which had probed the “cis effect” caused by

fluorine substitution in a *cis* position across a carbon–carbon double bond. Initially, Craig and Entemann¹ measured the enthalpy of isomerization of 1,2-difluoroethylene, which first revealed surprisingly that the *cis* isomer was $(928 \pm 38 \text{ kcal mol}^{-1})$ lower in energy than the *trans* isomer. To our knowledge, this remains the only measurement of the effect of fluorine substitution at the 1 and 2 positions on the enthalpy of isomerization of 1,2-difluoroethylene or any other olefin.

In 1964, Schlag and Kaiser¹⁰ measured the rate constant and the enthalpy of reaction for the *trans* to *cis* isomerization of octafluoro-2-butene. Measurements of the equilibrium constant of this isomerization showed that the *trans* isomer is $817(\pm 66) \text{ cal mol}^{-1}$ lower in energy than the *cis* isomer. Thus, this molecule does not exhibit a fluorine “cis effect” directly. However, because the van der Waals radius of CF_3 is substantially larger than that of CH_3 ,²³ Schlag and Kaiser postulated that the “cis effect” was masked by the increased steric destabilization of the *cis* isomer by the concomitant presence of *cis* CF_3 groups. These experiments further showed that the activation energy for the *trans* to *cis* isomerization reaction was $+56\,430 (\pm 250) \text{ cal mol}^{-1}$, much smaller than that for the *trans* to *cis* isomerization of 2-butene ($64\,993 \pm 1100 \text{ cal mol}^{-1}$) determined in Figure 1 and confirmed in Figure 2. Schlag and Kaiser postulated that the lowered activation energy is a result of a weakening of the π bond, which is broken during the isomerization process. The activation energy of the *trans* to *cis* isomerization of octafluoro-2-butene was subsequently verified by Jeffers ($56\,500 \pm 1900 \text{ cal mol}^{-1}$),²⁴ who used a relative rate measurement with *cis*-2-butene as the reference species. Once again, the Jeffers rate constant presented in Table 6 has been adjusted on the basis of the *cis*-2-butene rate constant presented in section 3.1.

Jeffers also measured the rate constant for the *cis* to *trans* isomerization of *cis*-1,2-difluoroethylene in two separate experiments,^{14,25} the results of which are included in Table 6 (adjusted for the current 2-butene rate constant). Unfortunately, as Jeffers notes,¹⁴ the two determinations do not agree even at the maximum of the combined error limits. Therefore, we believe they are of limited use in this discussion.

4.1.1. Incorporation of the Current Measurements.
4.1.2. Enthalpies of Isomerization. Our measurements are

Table 6. Summary of Thermodynamic and Kinetic Parameters of the Z to E (and E to Z Where Available) Isomerization of Fluoro-Olefins^a

reaction	ΔH (cal mol ⁻¹)	ΔS (eu)	A (s ⁻¹)	E_a (cal mol ⁻¹)	ref
(1) $Z\text{-CF}_3\text{CF=CHF} \rightarrow E\text{-CF}_3\text{CF=CHF}$	$+2845 \pm 100^a$	$+0.74 \pm 0.20$		$+62\,375 \pm 1000$	<i>b</i>
(-1) $E\text{-CF}_3\text{CF=CHF} \rightarrow Z\text{-CF}_3\text{CF=CHF}$			$10^{13.87 \pm 0.24}$	$+59\,530 \pm 887$	this work
(2) $Z\text{-CF}_3\text{CH=CHCF}_3 \rightarrow E\text{-CF}_3\text{CH=CHCF}_3$	-4330 ± 120	$+1.27 \pm 0.23$	$10^{13.89 \pm 0.23}$	$+58\,845 \pm 675$	this work
(-2) $E\text{-CF}_3\text{CH=CHCF}_3 \rightarrow Z\text{-CF}_3\text{CH=CHCF}_3$				$+63\,175 \pm 800$	<i>c</i>
(3) $Z\text{-CH}_3\text{CH=CHCH}_3 \rightarrow E\text{-CH}_3\text{CH=CHCH}_3$	<i>f</i>		$10^{13.95 \pm 0.23}$	$+63\,245 \pm 815$	this work
(-3) $E\text{-CH}_3\text{CH=CHCH}_3 \rightarrow Z\text{-CH}_3\text{CH=CHCH}_3$			$10^{14.32 \pm 0.28}$	$+64\,993 \pm 1132$	this work
$Z\text{-CF}_3\text{CF=CFCF}_3 \rightarrow E\text{-CF}_3\text{CF=CFCF}_3$				$+55\,613 \pm 250$	10
$E\text{-CF}_3\text{CF=CFCF}_3 \rightarrow Z\text{-CF}_3\text{CF=CFCF}_3$	$+817 \pm 66$	-0.486 ± 0.045	$10^{13.53 \pm 0.17}$	$+56\,430 \pm 250$	10 ^d
			3.4×10^{13}	$+56\,500 \pm 1900$	24
$Z\text{-CHF=CHF} \rightarrow E\text{-CHF=CHF}$	$+928 \pm 28^e$	$+0.134 \pm 0.064^e$			1
			6.5×10^{12}	$+57\,996 \pm 3000$	14
			3.6×10^{13}	$+64\,445 \pm 2500$	25

^aAll error limits in this table are 2σ . ^bZ to E activation energy is derived from the measured E_a of the E to Z isomerization reaction combined with the measured ΔH for the Z to E reaction. ^cE to Z activation energy is derived from the measured E_a and ΔH of the Z to E isomerization reaction. ^dReference reported the error limits as twice the “probable error”. The error limits have been changed to 2σ in Table 6. ^eNo error limits were quoted by Craig and Entemann. The error in this table represents 2σ derived from the same data by Craig, N. C.; Overend, J. J. *Chem. Phys.* **1969**, *51*, 1127–1142. ^fThe Z to E enthalpy of isomerization for 2-butene varies from approximately $-1000 \text{ cal mol}^{-1}$ at 298 K to $-500 \text{ cal mol}^{-1}$ at 800 K.¹⁷

designed to fill three specific gaps in the sparse existing data. First, the isomerization measurements on $\text{CF}_3\text{CF}=\text{CHF}$ provide the opportunity to examine a “cis effect” in a molecule other than 1,2- $\text{C}_2\text{F}_2\text{H}_2$, essentially doubling the experimental database on this phenomenon. Second, the study of $\text{CF}_3\text{CH}=\text{CHCF}_3$ allows a direct measurement of the CF_3 steric hindrance destabilization of the $Z(\text{cis})$ isomer relative to the $E(\text{trans})$ without the presence of F atoms on the double bond. These data can aid in the interpretation of the prior octafluoro-2-butene data. Finally, the study of these two molecules provides additional experimental data on the effect of both CF_3 and F atom substitution on the energetics of a $\text{C}=\text{C}$ double bond, which supplement the $\text{CF}_3\text{CF}=\text{CFCF}_3$ experiments of Schlag and Kaiser¹⁰ and Jeffers.²⁴

The Z to E enthalpy of isomerization of $Z\text{-CF}_3\text{CH}=\text{CHCF}_3$ [$\Delta H_2 = (-4330 \pm 120) \text{ cal mol}^{-1}$] shows that the $Z(\text{cis})$ isomer lies $4330 \text{ cal mol}^{-1}$ higher in energy than the $E(\text{trans})$ isomer. It is reasonable to assume that there is little steric interaction between the CF_3 group and a hydrogen atom in the E configuration and no interaction between H atoms in the Z configuration. On the basis of these assumptions, we arrive at the conclusion that steric repulsion between the CF_3 groups destabilizes the Z isomer by $4330 \text{ cal mol}^{-1}$. The measured enthalpy of isomerization of $E\text{-CF}_3\text{CF}=\text{CFCF}_3$ to its Z isomer is $(+817 \pm 66) \text{ cal mol}^{-1}$.¹⁰ Again, we assume there is little steric interaction between the CF_3 group and F atom in the E isomer and also little steric repulsion of the F atoms at the 2 and 3 positions in the Z isomer as opposed to the “cis effect” caused by these F atoms. The effect of the CF_3 steric interaction in the Z isomer can then be subtracted, giving an estimation of the “cis effect” in $Z\text{-CF}_3\text{CF}=\text{CFCF}_3$ $(+817 - 4330 = -3513 \pm 190) \text{ cal mol}^{-1}$. This represents an estimate of the stabilization produced by cis positioning of the two fluorine atoms across the double bond in $\text{CF}_3\text{CF}=\text{CFCF}_3$, subject to the assumptions stated above.

The enthalpy of isomerization of $Z\text{-CF}_3\text{CF}=\text{CHF}$ to the E isomer is $\Delta H_1 = +2843 \pm 100 \text{ cal mol}^{-1}$ as presented in Table 6. This indicates that the Z (fluorine cis) isomer is lower in energy than the E (fluorine trans) isomer by $2843 \text{ cal mol}^{-1}$. On the basis of the assumed lack of steric interactions between the CF_3 group and either the F or H atom across the double bond discussed above, this molecule shows a pronounced “cis effect” energy reduction of the Z isomer equal to $2843 \text{ cal mol}^{-1}$ relative to the E isomer. The “cis effect” stabilization relative to the trans isomer caused by the cis orientation of the F atoms in these two olefins ($Z\text{-CF}_3\text{CF}=\text{CHF}$ and $Z\text{-CF}_3\text{CF}=\text{CFCF}_3$) is similar $(-2843 \pm 100$ and $-3513 \pm 190 \text{ cal mol}^{-1}$, respectively), differing by $670 \pm 290 \text{ cal mol}^{-1}$. However, it is 3–4 times larger than the cis stabilization observed for *cis*-1,2-difluoroethylene ($928 \pm 38 \text{ cal mol}^{-1}$). We hope that others skilled in ab initio theoretical investigations will use these data to obtain additional insight into the “cis effect”.

There have been several ab initio studies of the cis stabilization in 1,2-difluoroethylene, which are summarized by Bannerjee et al. (see Table 5 of ref 3). The agreement between calculation and experiment depends on the level of theory used and the basis set chosen, but the best calculations agree well with the experimental value. To our knowledge, only one ab initio investigation of enthalpies of isomerization of larger fluoro-olefins has been carried out to date. Borisov et al.²⁶ calculated the total energies of the cis and trans isomers of 1,2-difluoroethylene, $\text{CF}_3\text{CH}=\text{CHCF}_3$, and $\text{CF}_3\text{CF}=\text{CFCF}_3$ (see

Table 2 in that publication). Borisov et al. present the calculated total energies at two levels of theory: MP2/6-31G* and MP2/aug-cc-pVDZ. They also provide the zero point vibrational corrections (at the RHF/6-31G* level of theory), which must be applied for rigorous comparison to the experimental data. For 1,2- $\text{C}_2\text{F}_2\text{H}_2$, the *cis* (ZPVE) minus the *trans* (ZPVE) = $+0.25 \text{ kcal mol}^{-1}$. This ZPVE correction is close to those calculated by Bannerjee et al. by various methods, deviating by less than $0.04 \text{ kcal mol}^{-1}$. The ZPVE-corrected enthalpies of the *cis* to *trans* isomerization of 1,2- $\text{C}_2\text{F}_2\text{H}_2$ calculated by Borisov et al. are $-0.69 \text{ kcal mol}^{-1}$ (MP2/6-31G*); and $+0.57 \text{ kcal mol}^{-1}$ (MP2/aug-cc-pVDZ). Thus, only at the MP2/aug-cc-pVDZ level of theory is the *cis* isomer predicted to be lower in energy than the *trans*.

For $\text{CF}_3\text{CF}=\text{CFCF}_3$ the *trans* isomer is calculated by Borisov et al.²⁶ to be the lower in energy at both levels of theory, with the *trans* to *cis* enthalpy of isomerization = $+0.5 \text{ kcal mol}^{-1}$ using the MP2/aug-cc-pVDZ theory level. The calculated ZPVE of both isomers is the same, and no correction is needed. The agreement between the ab initio calculation (MP2/aug-cc-pVDZ) of the enthalpy of isomerization ($+0.5 \text{ kcal mol}^{-1}$) and the observed value ($+0.817 \pm 0.07 \text{ kcal mol}^{-1}$) for *trans* to *cis* octafluoro-2-butene isomerization presented in Table 6 is certainly satisfactory.

For $\text{CF}_3\text{CH}=\text{CHCF}_3$, the entries in Table 2 of the Borisov et al.²⁶ publication indicate that the *trans* isomer is lower in energy by $\sim 5 \text{ kcal mol}^{-1}$ at the MP2/6-31G* level, but at the MP2/aug-cc-pVDZ level of theory the *cis* isomer is the lower in energy by $\sim 3.7 \text{ kcal mol}^{-1}$. Because the MP2/aug-cc-pVDZ level gave a result that was in total disagreement with the experimental results in Table 6, which showed the *trans* isomer to be the lower in energy, we contacted Dr. Borisov. He provided corrected values for the total energies of *cis*- and *trans*- $\text{CF}_3\text{CH}=\text{CHCF}_3$ for the MP2/aug-cc-pVDZ level of theory. The corrected values are $E_1(\text{cis}) = -751.1023212 \text{ au}$ and $E_1(\text{trans}) = -751.1107371 \text{ au}$.²⁷ Using these corrected energies at the MP2/aug-cc-pVDZ level of theory with the ZPVE corrections from Table 2 in Borisov et al., the *trans* isomer is predicted to be lower in energy than the *cis* isomer. The *cis* to *trans* enthalpy of isomerization of $\text{CF}_3\text{CH}=\text{CHCF}_3$ based on these corrected energies and the ZPVE correction in Table 2 of Borisov et al. is $-5.09 \text{ kcal mol}^{-1}$. This agrees reasonably well with the experimental value of $-4.33 \pm 0.12 \text{ kcal mol}^{-1}$ presented in our Table 6 and discussed in section 3.3.2, but we are not qualified to comment on the expected accuracy of ab initio calculations.

4.1.3. Activation Energies of the Fluoro-Olefin Isomerizations. To this point, the effect of fluorine substitution on a double bond has been discussed from a thermodynamics perspective, in which the objective is to observe and to attempt to explain the effect of cis fluorine atoms on the thermodynamics of the *cis*/*trans* isomers. Measurement of the isomerization rate constants provides a different perspective by examining the effect of fluorine substitution on the activation energy of the isomerization process. The activation energies of the isomerization rate constants for the olefin species are also presented in Table 6. In ref 10, Schlag and Kaiser suggest that the activation energy of isomerization provides a measure of the π bond uncoupling energy in an olefin since, in the transition state, there should be little overlap of the p orbitals on the olefinic carbons. It is possible, even probable, that the σ bond energy may also differ in the transition state as a result of a change of bond length. It seems

likely that the main difference in energy is from the breakage of the double bond, but this can only be explored through ab initio calculations of the entire reaction path including the transition state, which is beyond the scope of this work. In what follows, the effect of F or CF₃ substituents on the isomerization kinetics of the carbon–carbon double bond will be examined.

Activation energies of the trans to cis isomerization reactions will be compared since the trans species are not perturbed by the “cis effect” stabilization caused by fluorine atoms located cis to one another across the double bonded carbons. Also, the activation energies of the trans isomers are not perturbed by steric interactions of the methyl or trifluoromethyl groups located cis to one another. For these reasons, the trans to cis isomerization gives the best estimate of the energy involved in uncoupling a π bond. The baseline reaction for determining the effect of F atom substitution on the activation energy of trans to cis isomerizations is reaction –3, the trans to cis isomerization of *E*-2-butene. The activation energy of that reaction is $E_a(-3) = +64\,993 \pm 1130$ cal mol^{–1}, based on data in Figures 1 and 2, which are summarized in Table 6.

The activation energy for the *E* to *Z* isomerization of CF₃CH=CHCF₃ is $E_a(-2) = (+63\,175 \pm 800)$ cal mol^{–1}, which is 1818 ± 1930 cal mol^{–1} lower than that of *E*-2-butene. On the basis of this result, substitution of two, trans-located, trifluoromethyl groups across the double bond does not change the activation energy for the trans to cis isomerization to within the combined maximum error limits. However, a small decrease may be present since the overlap is at the maximum of the error limits.

The activation energy for isomerization of *E*-CF₃CF=CHF is $E_a(-1) = +59\,530 \pm 897$ cal mol^{–1}. This is significantly lower (by 5463 ± 2027 cal mol^{–1}) than that of 2-butene. The activation energy of *E*-CF₃CF=CFCF₃ ($+56\,430 \pm 250$ cal mol^{–1}) is 8563 ± 1380 cal mol^{–1} less than that of *E*-2-butene and 3100 ± 1137 less than that of *E*-CF₃CF=CHF.

In summary, the presence of CF₃ at each end of a double bond may produce a slight lowering of the uncoupling energy of the π bond, but any such effect is of the order of the experimental error. Fluorine atom substitution at each end of a double bond does result in a significant lowering of the activation energy for the isomerization process. However, because the activation energy of *E*-CF₃CF=CFCF₃ is significantly smaller than that of *E*-CF₃CF=CHF, the lowering of the energy necessary to uncouple the π bond must involve other factors in addition to the presence of F atoms on the ends of the double bond.

5. SUMMARY AND CONCLUSIONS

The effect of fluorine atom substitution at both ends of double bonded carbons has been examined with respect to the thermodynamics and kinetics of trans to cis (or cis to trans) isomerization reactions. The species studied were chosen to broaden the database for study of the “cis effect” produced by cis oriented fluorine atoms on opposite ends of the double bond. Such substitution results in the fluorine-cis (*Z*) isomer being lower in energy than the trans contrary to conventional wisdom, in which steric interaction between cis substituents results in the trans isomer being lower in energy. The following is a summary of the results.

1. The equilibrium constants for the *Z* to *E* isomerization of CF₃CF=CHF ($K_1 = 1.45(\pm 0.15)e^{-[2845(\pm 100)/RT]}$) and of CF₃CH=CHCF₃ ($K_2 = 1.9(\pm 0.22)e^{+[4330(\pm 120)/RT]}$) were measured from near ambient to 850 K using thermal

isomerization at high temperature and Cl catalyzed isomerization at lower temperature. The enthalpy of isomerization was determined from the equilibrium constant expressions as a function of temperature. The results showed that the *Z* (fluorine cis) isomer of CF₃CF=CHF is lower in energy than the *E* (fluorine trans) isomer by 2843 ± 100 cal mol^{–1}. This fluorine “cis effect” is much larger than the benchmark “cis effect” for 1,2-difluoroethylene used in ab initio investigations of this phenomenon, whose cis isomer is lower in energy by only 928 ± 38 cal mol^{–1}. As expected, no measurable “cis effect” is observed for CF₃CH=CHCF₃, which has no F substitution at the double bond. The *E*(trans) isomer of CF₃CH=CHCF₃ is lower in energy than the *Z*(cis) by 4330 ± 120 cal mol^{–1} because of the destabilizing steric interaction of the two relatively large CF₃ groups.

2. The measurement of the steric interaction between the CF₃ groups in *Z*-CF₃CH=CHCF₃ allows a more complete interpretation of the measured *E*(trans) to *Z*(cis) enthalpy of isomerization of CF₃CF=CFCF₃ reported in an earlier article ($+817 \pm 66$ cal mol^{–1}).¹⁰ In this case, the *E*(trans) isomer is lower in energy than the *Z*(cis), and it would appear that there is no “cis effect” in the case of the *Z* isomer. However, in this molecule, when the F atoms are in a cis orientation, the CF₃ groups are also cis to one another. Correcting for the destabilization produced by these CF₃ groups in CF₃CH=CHCF₃ ($=4330 \pm 120$ cal mol^{–1}), the cis fluorines in CF₃CF=CFCF₃ actually produce “cis effect” stabilization of the cis relative to the trans isomer equal to 3513 ± 190 cal mol^{–1}. The magnitude of this “cis effect” is also substantially larger than that observed for 1,2-difluoroethylene but similar to the “cis effect” in CF₃CF=CHF presented in conclusion 1.

3. The absolute rate constant for the cis to trans isomerization of 2-butene (k_3) was measured during these experiments over the temperature range 750–875 K. This rate constant has been measured several times before, and the measurement was repeated during these experiments to test our experimental method and temperature calibration. An extrapolation of our rate constant ($k_3 = 10^{13.95 \pm 0.23} e^{-63245(\pm 815)/RT}$ s^{–1}) agrees to within $\pm 10\%$ with the four previous measurements, which span the temperature range 680–1200 K. We believe that the fit to our data confirmed by the four separate determinations represents the best value of this rate constant to date.

4. The rate constants for the isomerizations of *Z*-CF₃CH=CHCF₃ ($k_2 = 10^{13.89 \pm 0.23} e^{-58845(\pm 675)/RT}$ s^{–1}) and *E*-CF₃CF=CHF ($k_{-1} = 10^{13.87 \pm 0.24} e^{-59530(\pm 887)/RT}$ s^{–1}) were measured at temperatures from 680 to 850 K. The rate constants of the *Z* to *E* isomerization of CF₃CF=CHF and the *E* to *Z* isomerization of CF₃CH=CHCF₃ were derived from the above expressions using the measured enthalpies of reaction. The activation energies of the *E* isomers when compared with that of *E*-2-butene showed that the uncoupling energy of the π bond decreases upon fluorine substitution across the double bond.

5. The rate constants for the additions of Cl to the double bonds in CF₃CF=CHF and CF₃CH=CHCF₃ were measured in N₂ and O₂ diluent during this study. These experiments showed that the Cl adduct is unstable with respect to dissociation in N₂ in verifying that this Cl addition can be used to catalyze the isomerizations effectively.

These measurements provide new data on the fluorine “cis effect” and on the effect of the presence of fluorine substitution on the double bond uncoupling energy. We hope that these new data will encourage additional ab initio calculations leading

to an improved understanding of the effect of fluorine atoms on the energetics of carbon–carbon double bonds.

■ APPENDIX. CF₂CL₂ STABILITY AND RATE CONSTANTS FOR CL + OLEFIN REFERENCE GASES

While it cannot react with Cl atoms, to be useful as an internal calibration species, CF₂CL₂ must also be thermally stable under the conditions studied. It does decompose thermally at very high temperature. Kumaran et al.²⁸ performed shock tube studies of CF₂CL₂ at ~350 Torr in the shocked gas over the temperature range 1450–2100 K and found that the decomposition to CF₂Cl + Cl followed a second order expression $1.35 \times 10^{-7} e^{-31663/T} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$ throughout the temperature range. Experiments at the lower temperatures where our experiments take place were not performed.

In our high-temperature reactor, two experiments were performed at 875 K specifically to test for thermal decomposition. The test mixture contained only CF₂CL₂ and N₂. Initially, 760 Torr of this mixture was placed in the reactor and withdrawn into the syringe after 80 s for injection into the GC. In the second experiment, 760 Torr was placed into the reactor and withdrawn after 620 s. Because there was no internal calibration species for this experiment, care was taken to fill the reactor to the same pressure to the best of our ability and to set the syringe at the same volume. Table 7 presents the

Table 7. Thermal Stability of CF₂CL₂

data set	T (K)	time (s)	peak area	source
1	876	80	8887	special experiment
		620	8838	
2	815	82	6889	Table 1, expt 2
		373	6807	
		15 120	5747	
3	751	1800	6809	Table 1, expt 1
		3600	6918	
		19 440	6978	
		60 660	6992	

results of this experiment as data set 1. In this table, the data are presented as integrated area counts from the FID detector system. As shown in Table 7, the fraction of CF₂CL₂ remaining after 620 s was 8838/8887 = 0.995 relative to that of the 80 s sample. The expected uncertainty is ~1.5%. Therefore, for a residence time of 540 s (620–80 s) at 875 K, any loss of CF₂CL₂ is less than the experimental uncertainty, and any measurement made at or below 875 K will not be affected significantly by CF₂CL₂ decomposition for reactor residence times less than 540 s. This covers ~2/3 of the measurements in Tables 1, 3, and 5. An upper limit to the low-pressure limiting rate constant for the decomposition reaction based on the estimated error limits of $\pm 1.5\%$ is $k < (\ln(0.985))/(-540[M])$, where the gas density $[M] = 8.3 \times 10^{18} \text{ molecules cm}^{-3}$. Thus, $k < 3.4 \times 10^{-24} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$. Evaluating the rate constant expression of Kumaran et al. at 875 K and 1 atm gives $2.6 \times 10^{-23} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$, which agrees with our upper limit reasonably well considering the measurements by Kumaran et al. were at temperatures 575–1275 K higher.

Two additional data sets were obtained from 2-butene isomerization experiments at 815 and 751 K in which the filling and sampling conditions were also closely controlled. At 815 K, one experiment had a sufficiently long residence time to

observe a definite decrease in FID signal. This data set is labeled experiment 2 in Table 7. Approximately 16% of the CF₂CL₂ decomposed after 15 120 s, a time and temperature combination that was never reached in any of the isomerization rate constant experiments. At 751 K (experiment 3 in Table 1), there was no decomposition observed after 60 660 s. The data in Table 7 span the conditions encountered in the isomerization experiments. They prove that CF₂CL₂ is stable under the varied conditions studied herein and, therefore, is a suitable internal calibration species for the high-temperature GC experiments.

The rate constant expressions for the reference species in the Cl atom relative rate experiments are as follows ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): Cl + C₂H₆ (at 297 K, 5.9×10^{-11} ; at elevated T, $[7.23 \times 10^{-13} T^{0.7} e^{+117/T}]^{29}$); Cl + C₂H₅Cl ($2.34 \times 10^{-11} e^{(-310/T)}$);³⁰ Cl + CH₃Cl ($4.0 \times 10^{-14} T^{0.92} e^{(-795/T)}$);³¹ Cl + CFCl₂H ($1.14 \times 10^{-22} T^{3.49} e^{(-241/T)}$);³² Cl + CF₃CFH₂ [HFC 134a] ($2.13 \times 10^{-12} e^{(-2165/T)}$);³³ Cl + CH₄ ($5.69 \times 10^{-19} T^{2.49} e^{-609/T}$).³¹ A selection of rate constants is required in relative rate constant measurements covering the range of rates to be studied for the species of interest. For example, if the reference has a rate constant 100 times smaller than the species of interest, consumption of 90% of the species of interest will result in ~2% consumption of the reference, which cannot be measured accurately.

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Notes

The authors declare no competing financial interest.

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