Substituent Effects on the Disproportionation– Combination Rate Constant Ratios for Gas-Phase Halocarbon Radicals, Part 5: Reactions of CF₃ + CF₃CH₂CHCH₃ and CF₃CH₂CHCH₃ + CF₃CH₂CHCH₃

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ABSTRACT: Rate constant ratios, k_d/k_c for the disproportionation/combination reaction have been measured as 0.07 ± 0.02 when an H is removed from the CH₂ position of the CF₃CH₂CHCH₃ radical and as 0.24 ± 0.03 when the H is removed from the CH₃ position in the reaction with the CF₃ radical. For the self-reaction between two CF₃CH₂CHCH₃ radicals, k_d/k_c has been measured as 0.27 ± 0.03 when the H is removed from the CH₂ position and as 0.47 ± 0.04 when the H is removed from the CH₃ position. The branching fraction, corrected for the number of hydrogens at each site, is 0.70 favoring the methyl position when the acceptor

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radical is CF₃ and 0.54 when CF₃CH₂CHCH₃ is the acceptor radical. Branching fraction results show that the CF₃ substituent on the CF₃CH₂CHCH₃ radical hinders disproportionation when CF₃ is the acceptor radical. When the accepting radical is CF₃CH₂CHCH₃ the CF₃ substituent may slightly impede the disproportionation reaction, but the branching ratio is nearly statistical. The effect of substituents on the donor radical, CF₃CH₂CHX, will be discussed for the series X = H, CF₃, Cl, and CH₃ when the acceptor radical is CF₃. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 33: 549–557, 2001

INTRODUCTION

For several years we have been investigating [1–4] reactions between halocarbon radicals by measuring the effect of substituents, with different electronic character, on the rate constant ratio of disproportionation versus combination, k_d/k_c . For these radicals the disproportionation reaction involves transfer of atomic hydrogen. Our method of producing the halocarbon radicals has been photolysis of hexafluoroacetone [5–7] or trifluoroacetic anhydride [4,8], which produces a CF₃ radical that subsequently adds to an alkene, CH₂=CYZ (reaction 1).

$$CF_3 + CH_2 = CYZ \longrightarrow CF_3CH_2CYZ$$
 (1)

By selecting specific alkenes, the CF_3CH_2CYZ radical can be formed with substituents at Y and at Z, which possesses specific inductive or steric characteristics. Advantages and limitations of this method have been discussed [2]. Using this method, we have studied the effects of changing Z from H to Cl to CF_3 while Y = H [1–3], and the effects of Y = Z = F [4].

Interpreting substituent effects, based upon the $k_{\rm d}/k_{\rm c}$, can be ambiguous because substituents can alter both the k_c and the k_d rate constants. Attempts to concurrently analyze the effects of substituents on k_c and k_d have had mixed success [1–4]. In order to extract information about the disproportionation reaction from $k_{\rm d}/k_{\rm c}$ ratios, assumptions about the steric or electronic factors affecting the rate of combination must be made. To alleviate the need to rationalize the effect of substituents on k_c , we will present a method whereby the effects of substituents on the disproportionation reaction will be directly determined by the branching ratio for disproportionation from two different sites on the same donor radical. This will be accomplished by generating a radical with two possible disproportionation pathways, such as the addition of a CF₃ radical to an alkene of the form $CHY = CHCH_2Z$.

$$CF_3 + CHY = CHCH_2Z \longrightarrow CF_3CHYCHCH_2Z$$
 (2)

For this discussion, the α -carbon of the CF₃CHYCHCH₂Z radical will be the carbon atom

with the CF₃ and the Y substituent, the β -carbon will be the carbon containing the radical electron, and the γ -carbon will be the carbon with the Z substituent. Both the α -carbon and the γ -carbon have hydrogen atoms which can be lost by disproportionation. The present work will be the first in the series with Y = Z = H and will determine the branching fraction and k_d/k_c when the CF₃CH₂CHCH₃ radical transfers an H from the CH₂ or CH₃ position. If CF₃CH₂CHCH₃ is viewed as (CF₃)CH₂CHCH₂(H), then the α - and γ -carbons each have two hydrogen atoms, but the third substitutent on the α -carbon is a CF₃ while at the γ -carbon it is an H atom; therefore, the branching fraction for disproportionation at these two carbons will determine the effect on the disproportionation reaction of a CF₃ substituent. The CF₃CH₂CHCH₃ radical will be prepared by the addition of CF_3 to the terminal end of the C=Cin propene [9].

Future studies could include comparison of the CF₃ substituent on the α -carbon with F, CH₃, CH₂CH₃, OH, and OCH₃ substituents on the γ -carbon. For example, addition of CF₃ radicals to 1-butene will form the CF₃CH₂CHCH₂CH₃ radical where the α -carbon has two transferable hydrogens and a CF₃ substituent while the γ -carbon has two transferable hydrogens and a CH₃ substituent. The branching fraction would provide a direct comparison of the effects of the CF₃ and CH₃ substituents, which are known to have very different electronic character.

EXPERIMENTAL METHODS

A mixture containing a total of 1.79μ mole of propene and hexafluoroacetone, with mole ratios varying from 1:15 to 15:1, were prepared on a grease-free glass vacuum line in either a 17.13 ml or a 32.07 ml quartz vessel, corresponding to pressures of 1.05 and 1.94 torr, respectively. Pressures were measured using an MKS 270 electronic manometer, and samples were photolyzed at room temperature for 4 min using a high pressure Oriel 6137 mercury lamp.

Products were identified by comparing retention times and mass spectra with those from authentic samples, or by mass spectral analysis when authentic samples were not available. Reactions 3-14 in the following section summarize the products anticipated for this study. Mass spectra (MS) were obtained for all major products by analyzing reaction mixtures on a Hewlett Packard 5890 Series II Gas Chromatograph with a 105 m by 0.25 mm Rtx-200 capillary column and a Hewlett Packard 5971 Series Mass Selective Detector. Commercial samples of $CH_2 = C(CF_3)CH_3$ and hexafluoroethane were purchased from PCR Inc. and CF₃CH=CHCH₃ (15% cis and 85% trans) was from Fluorochem Ltd. The $CH_2 = CHCH_2CF_3$ was prepared by photolysis [10] of CH₂=CHCH₂I (Aldrich Chemical) and CF₃I (PCR) in pyrex vessels containing Hg_2I_2 , and the $CH_3CH(CF_3)CH_3$ was prepared by the photolysis of CF₃I and CH₃CHICH₃ (Aldrich Chemical). A sample of 1,1,1-trifluorobutane was prepared by two synthetic routes, from the photolysis of CF3CH2I (PCR) and CH3CH2I, and also from the photolysis of CF₃I with CH₃CH₂CH₂I (Aldrich). These samples were used to verify identity of all products from the disproportionation reactions. For CH₃CH(CF₃)CH₂CH(CH₃)CH₂CF₃ CF₃CH₂CH(CF₃)CH₃, and (CF₃CH₂CHCH₃)₂ commercial samples were not available and no easy synthetic routes were known, and so the assignment was based upon the mass spectral results given in Table I and the following MS data. A parent ion peak was not present for CF₃CH₃CH(CF₃)CH₃, but a mass peak with

Table IMass Spectral Fragmentation Data at 70 eV(m/e and Relative Abundance)

m/e	R.A.	Assignment	
CF ₃ CH ₂ CH ₂	CH ₃		
92	100	$C_4F_2H_{6^+}$	
77	94.6	$C_{3}F_{2}H_{3^{+}}$	
29	86.0	$C_2H_{5^+}$	
64	69.7	$C_2F_2H_{2^+}$	
47	29.5	$C_2FH_{4^+}$	
27	25.7	$C_{2}H_{3^{+}}$	
trans-CF3CH	=CHCH ₃		
110	100	$C_4F_3H_{5^+}$	
41	54.1	$C_3H_{5^+}$	
64	48.9	$C_2F_2H_{2^+}$	
91	47.9	$C_4F_2H_{5^+}$	
39	44.7	$C_{3}H_{3^{+}}$	
77	27.7	$C_{3}F_{2}H_{3^{+}}$	
CF ₃ CH ₂ CH(CF ₃)CH ₃		
91	100	$C_4F_2H_{5^+}$	
47	44.3	$C_2FH_{4^+}$	
111	37.7	$C_4F_3H_{6^+}$	
77	30.7	$C_{3}F_{2}H_{3^{+}}$	
69	30.6	CF ₃₊	
64	23.1	$C_2F_2H_{2^+}$	

m/e	R.A. Assignm	
CH ₃ CH(CF ₃)	CH ₂ CH(CH ₃)CH ₂ CF ₃	
91	100	$C_4F_2H_{5^+}$
110	46.9	$C_4F_3H_{5^+}$
47	46.4	$C_2FH_{4^+}$
61	37.7	$C_3FH_{6^+}$
111	24.2	$C_4F_3H_{6^+}$
77	23.4	$C_{3}F_{2}H_{3^{+}}$
$CF_3CH_2CH =$	CH ₂	
110	100	$C_4F_3H_{5^+}$
41	67.1	$C_{3}H_{5^{+}}$
64	55.5	$C_2F_2H_{2^+}$
39	39.3	$C_{3}H_{3^{+}}$
77	26.7	$C_{3}F_{2}H_{3^{+}}$
91	19.9	$C_4F_2H_{5^+}$
<i>cis</i> -CF ₃ CH=0	CHCH ₃	
110	100	$C_4F_3H_{5^+}$
41	68.0	$C_{3}H_{5^{+}}$
64	62.4	$C_2F_2H_{2^+}$
39	55.2	$C_{3}H_{3^{+}}$
77	35.8	$C_{3}F_{2}H_{3^{+}}$
91	30.6	$C_4F_2H_{5^+}$
CF ₃ CH ₂ CH(C	$^{2}H_{3})CH(CH_{3})CH_{2}CF_{3}^{a}$	
91	100	$C_4F_2H_{5^+}$
110	77.7	$C_4F_3H_{5^+}$
47	29.0	$C_2FH_{4^+}$
111	19.5	$C_4F_3H_{6^+}$
139	18.4	$C_6F_3H_{10^+}$
77	18.3	$C_3F_2H_{3^+}$
CH ₃ CH(CF ₃)	CH ₃	
92	100	$C_4F_2H_{6^+}$
77	98.1	$C_{3}F_{2}H_{3^{+}}$
64	34.1	$C_2F_2H_{2^+}$
73	30.1	$C_4FH_{6^+}$
93	24.5	$C_4F_2H_{7^+}$
65	21.1	$C_2F_2H_{3^+}$

^{*a}Meso* and *d*,*l*-CF₃CH₂CH(CH₃)CH(CH₃)CH₂CF₃ were not completely resolved by the GC analysis and this is an average of both diasteriomers.</sup>

relative abundance of 6.4% at m/e = 161 corresponds to loss of F and a mass peak with relative abundance of 37.7% at m/e = 111 corresponds to loss of CF₃. Mass spectra for CH₃CH(CF₃)CH₂CH(CH₃)CH₂CF₃ and for *meso-* and *d*,*l*-(CF₃CH₂CHCH₃)₂ were very similar. The two mass spectra were distinguishable by the presence of CH₃CHCF₃⁺ in the spectrum for CH₃CH(CF₃)CH₂CH(CH₃)CH₂CF₃. The mass spectra for *meso-* and *d*,*l*-(CF₃CH₂CHCH₃)₂ were consistent with the fragmentation patterns we have found for other *meso-* and *d*,*l*-pairs [1–3].

Products were quantified using a Shimadzu GC-14A gas chromatograph equipped with a 105 m by 0.53 mm

Rtx-200 capillary column and a flame ionization detector. The column conditions were an initial temperature maintained at -15° C by cryo-cooling with liquid nitrogen for 35 min, followed by temperature programming at a rate of 20°C/min to a maximum temperature of 125°C. With these conditions, retention times in minutes were approximately as follows: 10.5 (CF₃CF₃), 11 (CH₃CH=CH₂), 21 (CH₂=C(CF₃)CH₃), 23 (CH₃(CF₃)CHCH₃), 24 (CF₃CH₂CH=CH₂), 27 (cis-CF₃CH=CHCH₃), 29 (CF₃CH₂CH₂CH₃), 31 (trans- $CF_3CH=CHCH_3$), 38 ($CF_3CH_2CH(CH_3)CF_3$), 51 (CH₃CH(CF₃)CH₂CH(CH₃)CH₂CF₃), and ((CF₃CH₂CHCH₃)₂). The meso- and d,l-stereoisomers for $(CF_3CH_2CHCH_3)_2$ were not completely resolved and so they were measured together. A Shimadzu Chromatopac CR5A integrator was used to collect data and integrate the peak areas. Calibration response factors(see Table II) for the flame ionization detector were determined for all butene products and they were estimated for the saturated products from previous work [4].

During the initial stages of this work, we noticed that when the concentrations of propene was small the CF₃ radical would preferentially attack the CF₃CH₂CH=CH₂ product but not the CF₃CH=CHCH₃ product. For this case, the butene ratio in Fig. 4 decreased as the percentage of propene decreased, and varied with the extent of photolysis. To eliminate this complication, the initial concentration of propene was increased, which serves to protect the product alkenes from attack by CF₃ radicals, and the photolysis times were reduced. These experimental conditions reduced the yield of secondary products, resulting from the CF₃ radical adding to the trifluorobutenes, to below our detection limit.

Table IIRelative Response Factors for the FID GasChromatograph Relative to $CF_3CH_2CH_2CH_3$

$CH_3(CF_3)C=CH_2$	1.05
$CH_2 = CHCH_2CF_3$	1.05
cis-CH ₃ CH=CHCF ₃	1.05
trans-CH ₃ CH=CHCF ₃	1.05
CF ₃ CH ₂ CH ₂ CH ₃	1.00
CF ₃ CH ₂ CH(CF ₃)CH ₃	1.11
CH ₃ CH(CF ₃)CH ₂ CH(CH ₃)CH ₂ CF ₃	2.00
(CF ₃ CH ₂ CHCH ₃) ₂	2.00

RESULTS AND DISCUSSION

The following reaction scheme summarizes the reactions involving the CF₃ and CF₃CH₂CHCH₃ radicals, formed by the addition of CF_3 to the CH_2 end of CH_3 =CHCH₃.

$$CF_{3} + CF_{3}CH_{2}CHCH_{3}$$

$$\stackrel{k_{d\alpha}}{\longrightarrow} CF_{3}H + CF_{3}CH = CHCH_{3}$$
(3)

$$CF_{3} + CF_{3}CH_{2}CHCH_{3}$$

$$\xrightarrow{k_{d\gamma}} CF_{3}H + CF_{3}CH_{2}CH = CH_{2} \qquad (4)$$

$$CF_{3} + CF_{3}CH_{2}CHCH_{3}$$
$$\xrightarrow{k_{c}} CF_{3}CH_{2}CH(CH_{3})CF_{3}$$
(5)

$$2 \operatorname{CF_3CH_2CHCH_3} \xrightarrow{k_{\mathrm{da'}}} \operatorname{CF_3CH_2CH_2CH_3} + \operatorname{CF_3CH=CHCH_3} (6)$$

$$2 \operatorname{CF_3CH_2CHCH_3} \xrightarrow{k_{\mathrm{dy'}}} \operatorname{CF_3CH_2CH_2CH_3} + \operatorname{CF_3CH_2CH=CH_2} (7)$$

$$2 \operatorname{CF_3CH_2CHCH_3} \xrightarrow{k_{c'}} (\operatorname{CF_3CH_2CHCH_3})_2 \quad (8)$$

A kinetic analysis for the rates of reactions 3–8, following the method of Cadman and Owen [11], gives the following equations:

(Ia)
$$R[CF_3CH=CHCH_3]/R[CF_3CH_2CH(CH_3)CF_3]$$

= $k_{d\alpha}/k_c + k_{d\alpha'}/k_{c'}R[(CF_3CH_2CHCH_3)_2]/R[CF_3CH_2CH(CH_3)CF_3]$

- (IIa) $R[CF_{3}CH=CHCH_{3}]/R[(CF_{3}CH_{2}CHCH_{3})_{2}]$ $= k_{d\alpha'}/k_{c'} + k_{d\alpha}/k_{c}$ $\times R[CF_{3}CH_{2}CH(CH_{3})CF_{3}]/$ $R[(CF_{3}CH_{2}CHCH_{3})_{2}]$
- (III α) $R[CF_3CH=CHCH_3]/R[CF_3CH_2CH_2CH_3]$ = $k_{d\alpha'}/(k_{d\gamma'} + k_{d\alpha'}) + k_{d\alpha}/k_c$ $\times R[CF_3CH_2CH_2CH_3]/R[CF_3CH_2CH_2CH_3]$
- (I γ) $R[CF_3CH_2CH=CH_2]/$ $R[CF_3CH_2CH(CH_3)CF_3]$ $= k_{d\gamma}/k_c + k_{d\gamma'}/k_{c'}R[(CF_3CH_2CHCH_3)_2]/$ $R[CF_3CH_2CH(CH_3)CF_3]$

(II
$$\gamma$$
) $R[CF_3CH_2CH=CH_2]/R[(CF_3CH_2CHCH_3)_2]$

- $= k_{d\gamma'}/k_{c'} + k_{d\gamma}/k_{c}$ × R[CF₃CH₂CH(CH₃)CF₃]/ R[(CF₃CH₂CHCH₃)₂]
- (III γ) $R[CF_3CH_2CH=CH_2]/R[CF_3CH_2CH_2CH_3]$ = $k_{d\gamma'}/(k_{d\gamma'} + k_{d_{\alpha'}}) + k_{d\gamma}/k_c$ $\times R[CF_3CH_2CH(CH_3)CF_3]/$ $R[CF_3CH_2CH_2CH_3]$

where R is the rate of product formation and the rate ratio is taken to be equivalent to the product yield ratio. A plot of the left-hand side of Eqs. $I\alpha$ -III γ versus the product ratio on the right-hand side of the equations should be linear, with a slope and an intercept giving specific k_d/k_c results for each equaton. The branching ratio for disproportionation, $k_{d\alpha}/k_{d\gamma}$, will be determined from a plot of [CF₃CH= $CHCH_3]/[CF_3CH_2CH=CH_2]$ versus the percentage of propene in the reaction mixture. When the percentage of propene approaches zero, reactions 3-5 will be dominant because $[CF_3] \gg [CF_3CH_2CHCH_3]$, but when the percentage of propene approaches 100, products from reactions 6-8 become relatively more important as the $[CF_3]/[CF_3CH_2CHCH_3]$ decreases. The $[CF_3]/[CF_3CH_2CHCH_3]$ is varied by changing the ratio of the two reactants from 1:15 to 15:1 and this causes the product yield ratios, shown in Figs. 1-4, to vary.

All the products shown in reactions 3–8 were observed; however, the presence of small amounts of secondary products suggested that CF_3 addition to the middle carbon of propene was also occurring. This is in agreement with results found by Tedder and coworkers [9], who observed the addition of CF_3 to the CH_2 end of CH_3 =CHCH₃ as the dominant pathway, with a 12:1 ratio of addition. Addition of CF_3 radicals to the central carbon of propene forms the $CH_2CH(CF_3)CH_3$ radical, which would undergo disproportionation and combination reactions with CF_3 and $CF_3CH_2CHCH_3$ radicals (reactions 9–14). The



Figure 1 Plots of the left-hand side versus the product ratio on the right-hand side of Eqs. I. The circles are for Eq. Iγ (the alkene product is the 4,4,4-trifluoro-1-butene isomer); the slope is $k_{d\gamma'}/k_{c'}$ and equals 0.45, the intercept is $k_{d\gamma}/k_c$ and equals 0.25, and the correlation coefficient is 0.951. The squares are for Eq. I α (the alkene product is the sum of the *cis*- and *trans*-1,1,1-trifluoro-2-butene isomers); the slope is $k_{d\alpha'}/k_c$ and equals 0.26, the intercept is $k_{d\alpha}/k_c$ and equals 0.074, and the correlation coefficient is 0.986.



Figure 2 Plots of the left-hand side versus the product ratio on the right-hand side of Eqs. II. The circles are for Eq. II γ (the alkene product is the 4,4,4-trifluoro-1-butene isomer); the slope is $k_{d\gamma}/k_c$ and equals 0.22, the intercept is $k_{d\gamma'}/k_{c'}$ and equals 0.48, and the correlation coefficient is 0.874. The squares are for Eq. II α (the alkene product is the sum of the *cis*- and *trans*-1,1,1-trifluoro-2-butene isomers); the slope is $k_{d\alpha'}/k_c$ and equals 0.27, and the correlation coefficient is 0.915.

concentration of $CH_2CH(CF_3)CH_3$ radicals is so small compared to CF_3 and $CF_3CH_2CHCH_3$ radicals that collisions between two $CH_2CH(CF_3)CH_3$ radicals can be ignored.

$$CF_3 + CH_2CH(CF_3)CH_3$$

$$\xrightarrow{k_d} CF_3H + CH_2 = C(CF_3)CH_3 \qquad (9)$$



Figure 3 Plot of the left-hand side versus the product ratio on the right-hand side of Eq. III. The circles are for Eq. III γ (the alkene product is the 4,4,4-trifluoro-1-butene isomer); the slope is $k_{d\gamma}/k_c$ and equals 0.23, the intercept is 0.678, and the correlation coefficient is 0.823. The squares are for Eq. III α (the alkene product is the sum of the *cis*- and *trans*-1,1,1trifluoro-2-butene isomers); the slope is $k_{d\alpha}/k_c$ and equals 0.056, the intercept 0.40, and the correlation coefficient is 0.812.



Figure 4 Plots of the ratio of trifluorobutene isomers versus the percentage of propene in the reaction mixture. The squares are for *cis*-1,1,1-trifluoro-2-butene/*trans*-1,1,1-trifluoro-2-butene and is constant at 0.183. The circles are for 4,4,4-trifluoro-1-butene/1,1,1-trifluoro-2-butenes and decreases from about 3 to 1.8 as the relative amount of propene increases.

$$CF_3 + CH_2CH(CF_3)CH_3$$
$$\xrightarrow{k_c} CF_3CH_2CH(CH_3)CF_3$$
(10)

 $CH_2CH(CF_3)CH_3+CF_3CH_2CHCH_3$

$$\xrightarrow{\kappa_{dl'}} CF_3CH_2CH_2CH_3 + CH_2 = C(CF_3)CH_3 \quad (11)$$

$$CH_{2}CH(CF_{3})CH_{3} + CF_{3}CH_{2}CHCH_{3}$$
$$\xrightarrow{k_{d2'}}CH_{3}CH(CH_{3})CF_{3} + CF_{3}CH=CHCH_{3}$$
(12)

 $CH_{2}CH(CF_{3})CH_{3} + CF_{3}CH_{2}CHCH_{3}$ $\xrightarrow{k_{d3'}} CH_{3}CH(CH_{3})CF_{3} + CF_{3}CH_{2}CH = CH_{2} \quad (13)$ $CH_{2}CH(CF_{3})CH_{3} + CF_{3}CH_{2}CHCH_{3}$

$$\xrightarrow{k_{c'}} CF_3CH_2CH(CH_3)CH_2CH(CH_3)CF_3$$
(14)

The $CH_2 = C(CF_3)CH_3$ formed by reactions 9 and 11, the CH₃CH(CH₃)CF₃ formed by Reactions 12 and 13, and the recombination product in reaction 14 are not formed by reactions 3-8 and so their presence will not affect the kinetic analysis leading to Eqs. $I\alpha$ -III γ . The 1- and 2-trifluorobutene yields from reactions 3, 4, 6, and 7 would be augmented by reactions 12 and 13, respectively. The yield of CH₃CH(CH₃)CF₃, from reactions 12 and 13, equals the sum of the yield of the extra 1- and 2-butene from the same reactions. The yield of CH₃CH(CH₃)CF₃ was always very low, but if it was observed, those experiments were discarded and we are confident that the measured trifluorobutene yield is only from reactions 3, 4, 6, and 7. The presence of reaction 11 would add to the CF₃CH₂CH₂CH₃ yield from reactions 6 and 7. We could measure the yield of $CH_2 = C(CF_3)CH_3$ from reaction 11, and its yield must equal the CF₃CH₂CH₂CH₃ yield from the same

reaction. In all trials reported in Figs. 1–3, the yield of $CH_2=C(CF_3)CH_3$ was less than 1.5% of the total 1- and 2-trifluorobutene yield, and so we do not believe that the production of $CF_3CH_2CH_2CH_3$ via reaction 11 significantly alters the analysis. Reactions 5 and 10 both produce $CF_3CH_2CH(CH_3)CF_3$; we estimate that the presence of reaction 10 introduces no more than a 10% uncertainty in the $CF_3CH_2CH(CH_3)CF_3$ concentration as compared to that from reaction 5, because Tedder and coworkers [9] found that the $CH_2CH(CF_3)CH_3CH_2CH(CH_3)CF_3$. Thus, reactions 9–14 can be ignored.

Another complication could arise because the $CF_3CH_2CHCH_3$ radical is chemically activated by reaction 2. The energized CF₃CH₂CHCH₃ radical could react by H-migration or by elimination of atomic hydrogen or HF. Elimination of HF leads to products not found in Eqs. 3-8 and so this can be ignored. We have previously tested [2,3] for rearrangement of smaller radicals and found that none occurred. The lack of H-migration is not surprising because the CF₃CH₂CHCH₃ radical is a secondary one and rearrangement would lead to a primary radical that would be more stable. Experimental thermochemical data are not available for all the radicals, but using density functional theory at the B3PW91/6-311 + G(2d,p) level we calculated that the CF₃CH₂CHCH₃ radical is the most stable and the possible rearrangement radicals are less stable; CF3CHCH2CH3 by 9.2 kJ/mol and CF₃CH₂CH₂CH₂ by 14.2 kJ/mol. We did use very small reaction vessels of different sizes, which would maximize and vary by nearly a factor of 2, the collisional stablization rate between the bath gas and the energized CF₃CH₂CHCH₃ radical. There was no evidence that the CF₃CH₂CHCH₃ radicals were undergoing unimolecular elimination of H or HF.

Product ratios were plotted for all six equations, Eqs. I α -III γ , to determine disproportionation/combination ratios. Figure 1 is a plot of the relative product yields of the left-hand side versus the relative product yields of the right-hand side of Eq. I. The intercepts of 0.074 and 0.25 represent $k_{d\alpha}/k_c$ and $k_{d\gamma}/k_c$, respectively, and the slopes of 0.26 and 0.45 represent $k_{d\alpha'}/k_{c'}$ and $k_{d\gamma'}/k_{c'}$, respectively. Figure 2 is a similar plot of Eqs. II with the intercepts of 0.27 and 0.48 representing $k_{d\alpha'}/k_{c'}$ and $k_{dv'}/k_{c'}$, respectively, and the slopes of 0.064 and 0.22 representing $k_{d\alpha}/k_c$ and $k_{d\gamma}/k_c$, respectively. Figure 3 is a plot of Eqs. III, with slopes equal to 0.056 $(k_{d\alpha}/k_c)$ and 0.23 (k_{dy}/k_c) , and intercepts equal to the disproportionation fractions, 0.40 $(k_{d\alpha'}/(k_{d\alpha'} + k_{d\gamma'}))$, for the squares and 0.68 $(k_{d\gamma'}/(k_{d\alpha'} + k_{d\gamma'}))$, for the circles. The two disproportionation fractions should add to 1, and the intercepts of Fig. 3 sum to 1.08 which is in good agreement with the expected value. The slope and intercept values from Figs. 1–3 are summarized in Table III and recommended values are given.

The rate constant ratio $k_{d\gamma}/k_{d\alpha}$ is determined by dividing $k_{d\gamma}/k_c$ by $k_{d\alpha}/k_c$, and using the recommended values in Table III gives a branching ratio of 3.4. Figure 4 shows the product ratio of [CF₃CH₂CH=CH₂]/[CF₃CH=CHCH₃] as a function of the mole percent of propene in the reaction mixture. As the concentration ratio of the reactants propene and hexafluoroacetone approaches 1:15, the percentage of propene in Fig. 4 approaches zero and $[CF_3] \gg [CF_3CH_2CHCH_3]$. For this case, reactions 3-5 become the dominant reactions and, at the limit of zero propene percentage, the $[CF_3CH_2CH=CH_2]/[CF_3CH=CHCH_3] = k_{d\gamma}/k_{d\alpha}.$ The [CF₃CH₂CH=CH₂]/[CF₃CH=CHCH₃] is increasing as the propene percentage declines and does appear to approach 3.4, which is consistent with the $k_{d\nu}/k_{d\alpha}$ based on results from Table III. We are unable to use a percentage of propene less than 6%, because the CF₃ radical begins to attack the alkene products. This causes the [CF₃CH₂CH=CH₂]/[CF₃CH=CHCH₃] in Fig. 4 to decrease, as the propene percentage approaches zero, because the CF₃ radical preferentially adds to the terminal alkene, CF₃CH₂CH=CH₂. The rate constant ratio $k_{d\gamma'}/k_{d\alpha'}$ is obtained from Table III by dividing the $k_{d\gamma'}/k_{c'}$ by $k_{d\alpha'}/k_{c'}$, which gives a ratio of 1.7. Reactions 6-8 become relatively more important as the initial propene composition in the reaction mixtures approaches 100%; that is the, concentration ratio of propene and hexafluoroacetone approaches 15:1, and the [CF₃CH₂CH=CH₂]/[CF₃CH=CHCH₃] in Fig. 4 should approach the $k_{d\gamma'}/k_{d\alpha'}$. In Fig. 4 the product yield ratio, as the propene percentage approaches 100, is 1.8 and is in excellent agreement with the 1.7 from the rate constant ratio. The importance of Fig. 4 is that the branching fraction is directlyrelated to the product ratio. These data should be more accurate because the calibration factors for the frame ionization detection (FID) are based upon the response for two geometric isomers versus the response for three to five different compounds that are required for Figs. 1-3. In addition, we can easily detect when CF₃ radicals are adding to the alkene products, which would be difficult to detect from the data in Figs. 1-3. Figure 4 also shows that the cis/trans ratio for CF₃CH= CHCH₃ is constant and averages to 0.183, similar to the 0.14 previously observed [1] for $CF_3CH=CHCl$ isomers produced by the disproportionation reaction between CF₃CH₂CHCl and CF₃ radicals.

Comparing the disproportionation/combination rate constant ratio when CF₃ removes an H from the γ -carbon of the CF₃CH₂CHCH₃ radical (0.24) versus CF₃CH₂CHCH₃ removing an H from the γ -carbon of the CF₃CH₂CHCH₃ radical (0.47) shows an increase by almost a factor of 2. A statistical factor of 2 results from the collision between two CF₃CH₂CHCH₃ radicals because either radical can donate or accept the hydrogen. A similar statistical factor of 2 was found in the earlier studies [2–4] for CF₃CH₂CHCl, CF₃CH₂CH₂, and CF₃CH₂CF₂ radicals. However, a factor of nearly 4 is found when CF₃ removes an H from the α -carbon of the CF₃CH₂CHCH₃ radical (0.07) versus CF₃CH₂CHCH₃ removing an H from the α -carbon of the CF₃CH₂CHCH₃ radical (0.27).

Our goal is to determine the effect of different substituents on the rate of disporportionation and to use that information to better understand the nature of substituent effects and the nature of the

	$CF_3{}^a$		CF ₃ CH ₂ CHCH ₃ ^a		
	$k_{ m d\alpha}/k_{ m c}$	$k_{\rm d\gamma}/k_{\rm c}$	$k_{\mathrm{d}lpha'}/k_{\mathrm{c}'}$	$k_{\mathrm{d}\gamma'}/k_{\mathrm{c}'}$	R^*
CF ₃ CH ₂ CHCH ₃ ^b					
Equation (I)	0.074		0.26		0.986
Equation (II)	0.064		0.27		0.915
Equation (III)	0.056		_		0.812
Recommended	0.07 ± 0.02		0.27 ± 0.03		
CF ₃ CH ₂ CHC H ₃ ^b					
Equation (I)		0.25		0.45	0.951
Equation (II)		0.22		0.48	0.874
Equation (III)		0.23		_	0.823
Recommended		0.24 ± 0.03		0.47 ± 0.04	

Table IIIExperimental Disproportionation/Combination Rate Constant Ratios and the Correlation Coefficient R*,from Figs. 1–3

^aRedicals accepting H.

^bDonor radicals, where the H that is being transferred is indicated by boldface.

transition state for disproportionation. This will be accomplished, in part, by comparing the disproportionation branching ratio, $k_{d\gamma}/k_{d\alpha}$, when an H is removed from the CH₃ position versus the CH₂ position of the CF₃CH₂CHCH₃ radical. This is a direct determination of the effect of the CF₃ substituent compared to H. To facilitate comparison, we will report the branching fraction for disproportionation at each of the two carbons corrected to account for the number of hydrogens available for transfer. If the rates are the same at the two sites of disproportionation then the branching fraction will be 0.50 at each carbon and any deviation from 0.50 will arise from substituent effects.

For the CF_3 reaction that removes an H from $CF_3CH_2CHCH_3$, disproportionation occurs at the γ carbon 3.4 times more frequently than at the α -carbon (see Table III). After adjustment for the number of H atoms at each carbon, the branching fraction per H atom, is 0.70 at the γ -carbon (the CH₃ end) and 0.30 at the α -carbon. The CF₃ substituent on the α -carbon clearly impedes disproportionation, relative to a hydrogen substitutent. This finding agrees with that of Fukui and coworkers [12], who used molecular orbital (MO) theory to predict that the transition state is polar for disproportionation and neutral for combination. The ab initio calculations [12] investigated disproportionation for the transfer of an H from the CH₂CH₃ radical to the CH₃ radical. According to the model, disproportionation proceeds by the C-H bond at the methyl end of the CH₂CH₃ radical (the donor radical) releasing electron density to the unpaired electron of the CH₃ radical (the acceptor radical). This release of electron density weakens the C-H bond of the methyl group on the ethyl radical to the point that the H is abstracted by the CH₃ radical, yielding methane and ethene. The model predicts that disproportionation will be retarded when the donating radical has an electronwithdrawing substituent and also when the acceptor radical has an electron-releasing substituent. Our experimental branching ratio shows that a CF₃ substituent on the donor radical reduces the rate of the disproportionation reaction by a factor of 2.3 when the acceptor radical is CF₃.

When the acceptor radical is changed from CF₃ to CF₃CH₂CHCH₃ the branching fractions are 0.46 \pm 0.05 at the α -carbon and 0.54 \pm 0.05 at the γ -carbon, when corrected for the number of H's on each carbon. The branching fraction is considerably different than when CF₃ is the accepting radical and it is now nearly statistical. Disproportionation may be slightly favored at the γ -carbon, but the variation from 0.46 to 0.54 is within the combined experimental uncertainty. Nearly identical results were found for the disproportionation of 2-butyl radicals. A statistical ratio of 1.5 has been reported [13,14] for the collision of two CH₃CH₂CHCH₃

radicals forming 1-butene versus cis- + trans-2butene. The most recent study finds a very slight preference for 2- butene formation for the collision of 2-butyl radicals [15]; $k_d/k_c = 0.14 \pm 0.01$ for 1-butene and 0.18 \pm 0.02 for cis- + trans-2-butene, when corrected for the number of available hydrogens.

For the reactions between two CF3CH2CHCH3 radicals, the acceptor radical contains groups (CF₃CH₂, CH₃, and H) that are electron releasing, at least compared to the three fluorines on the CF₃ radical. According to the ab initio calculations [12] these substituents should reduce the disproportionation rate, but not the branching ratio. Apparently, the disproportionation rate is reduced by different amounts at the two different sites on the donor radical. The donor radical contains a CF₃ group at the α -carbon and this electronrich substituent may repel an incoming CF₃ acceptor radical, but not a CF₃CH₂CHCH₃ radical that has a greater hydrocarbon-radical character. A similar trend has been observed by Pritchard and coworkers [16-20]. For example, when the donor radical was CHF_2 and the acceptor radical was changed from a perfluoro radical to an alkyl radical, k_d/k_c , for several acceptor radicals, varied as follows: 0.088 (CF₃), 0.072 (n-C₃F₇), 0.07 (CHF₂), 0.06 (CH₂F), 0.35 (CH₃), 0.37 (C₂H₅), and 0.30 (*n*-C₃H₇). The experimental k_d/k_c for CHF₂ was reduced by a statistical factor of 2 because the CHF₂ radical can be either the acceptor or the donor radical. Although Pritchard's data are for the disproportionation/combination rate constant ratio while our results are just for disproportionation, the trend does agree with our observation for just disproportionation.

Table IV gives disproportionation/combination rate constant ratios for the CF₃ radical accepting an H from the CH₂ position from a series of radicals of the form CF₃CH₂CHX, where X = H, Cl, CF₃, and CH₃. Since a substituent on the radical carbon should not greatly affect disproportionation, the disproportionation/combination rate constant ratios are all in the range 0.045 ± 0.025, but appears to increase for X =H, Cl, CF₃, and CH₃ in that order. Assuming that the disproportionation rates for CF₃ with CF₃CH₂CHCF₃

Table IVExperimental Disproportionation/Combination Rate Constant Ratios for CF_3 RadicalsAccepting an H from the CH_2 position on CF_3CH_2CHX Radicals (X = H, Cl, CF_3 , and CH_3)

Donor Radical	Acceptor Radical	$k_{\rm d}/k_{\rm c}$	Reference
CF ₃ CH ₂ CH ₂	CF ₃	0.022 ± 0.010	[2]
CF ₃ CH ₂ CHCl	CF ₃	0.037 ± 0.010	[1]
CF ₃ CH ₂ CHCF ₃	CF ₃	0.066 ± 0.020	[3]
CF ₃ CH ₂ CHCH ₃	CF ₃	0.07 ± 0.02	This work

and with CF₃CH₂CHCH₃ are the same, the combination rates must also be the same within our experimental error. This demonstrates that substituents' electronic natures are unimportant in combination reactions, because CH₃ and CF₃ are very different in electronic nature but similar in steric size [5]. This agrees with the MO calculations [12], which predicts that combination rates are not influenced by a substituent's electronic nature. The radical center is probably becoming more crowded as X changes along the series (X =H, Cl, CF₃, or CH₃), which might reduce the combination rate causing the k_d/k_c to increase. Rabinovitch and coworkers [21] have noted that steric hinderance may also influence the relative availability of the H atoms in disproportionation reactions; however, this would decrease the k_d/k_c , if the k_c remained constant, as the X changes along the series $X = H, Cl, CF_3$, and CH₃.

All the disproportionation/combination rate constants that we have previously measured [1-4] for fluorocarbon radicals have ranged between 0.022 and 0.125. When a CF₃ removes an H from the α -carbon of the CF₃CH₂CHCH₃ radical the k_d/k_c is within this range, but when the H is from the CH₃ position or when the CF₃CH₂CHCH₃ radicals self-disproportionate the values are much higher, 0.24-0.47. Pritchard and coworkers [17] also found that hydrocarbon acceptor radicals have much larger k_d/k_c ratios than perfluorocarbon radicals. As mentioned previously, Pritchard and coworkers [16-20] found that methyl, ethyl, and *n*-propyl radicals, accepting an H from CHF₂, all had $k_{\rm d}/k_{\rm c}$ near 0.3, whereas the $k_{\rm d}/k_{\rm c}$ values were between 0.06 and 0.09 when the acceptor radical was a $n-C_3F_7$ or a CF₃ radical.

CONCLUSIONS

Disproportionation/combination rate constant ratios have been measured as 0.07 ± 0.02 for the reactions of CF₃ with CF₃CH₂CHCH₃ radicals when the H is removed from the CH₂ position and as 0.24 ± 0.03 when the H is removed from the CH₃ position. For the selfreaction of CF₃CH₂CHCH₃ radicals, k_d/k_c is 0.27 ± 0.03 when the H is removed from the CH₂ position and 0.47 ± 0.04 when the H is removed from the CH₃ position. Comparison of a CF₃ substituent at the CH₂ position versus an H substituent at the CH₃ position, when the acceptor radical is CF₃, reveals that a CF₃ substituent hinders disproportionation, with only 30% of the total disproportionation occurring at the carbon with the CH₂. The results agree with predictions based on the MYFF model. Also, relative disproportionation/combination rate constant ratios were compared for CF₃ removing an H from the CH₂

position of CF₃CH₂CHX radicals and the relative rate constant ratio increased by about a factor of 3 as X changes from H to Cl, CF₃, and CH₃. One of the more surprising results is that the disproportionation rate constant nearly equals the combination rate constant when two CF₃CH₂CHCH₃ radicals collide; the $k_{d'}/k_{c'} = 0.74 \pm 0.05$ and this may reflect the steric influence of a bulky radical center on the combination rate constant.

BIBLIOGRAPHY

- 1. Holmes, B. E.; Rakestraw, D. J. Int J Chem Kinet 1987, 19, 401.
- McDowell, D. R.; Weston, J.; Holmes, B. E. Int J Chem Kinet 1996, 28, 61.
- McDowell, D. R.; Holmes, B. E. Int J Chem Kinet 1996, 28, 109.
- 4. Smith, S. R.; Holmes, B. E. Int J Chem Kinet 1999, 31, 237.
- Unger, S. H.; Hansch, C. Progr Phys Org Chem 1974, 12, 91.
- Ayscough, P. B.; Steacie, F. R. S. Proc R Soc London, Ser A 1954, 234, 476.
- 7. Gordon, A. S. J Chem Phys 1962, 36, 1330.
- 8. Watkins, P. E.; Whittle, E. J Chem Soc, Faraday Trans 2, 1984, 80, 2323.
- (a) Tedder, J. M.; Walton, J. C. Acc Chem Res 1976, 9, 183; (b) Tedder, J. M.; Walton, J. C. In ACS Symposium Series; Root, J. W. (Ed.); American Chemical Society: Washington, D.C.; 1978, pp. 66.
- Holmes, B. E.; Paisley, S. D.; Rakestraw, D. J.; King, E. E. Int J Chem Kinet 1986, 18, 639.
- Cadman, P.; Owen, H. L. J Chem Soc, Faraday Trans 1, 77, 1981, 3087.
- 12. Minato, T.; Yamabe, S.; Fujimoto H.; Fukui, K. Bull Chem Soc Jpn 1978, 51, 1.
- Kraus, J. W.; Clavert, J. G. J Am Chem Soc 1957, 79, 5921.
- Larson, C. W.; Rabinovitch, B. S. J Chem Phys 1969, 51, 2293.
- Falconer, W. E.; Sunder, W. A. Int J Chem Kinet 1971, 3, 523.
- Pritchard, G. O.; Abbas, S. H.; Kennedy, J. M.; Paquette, S. J.; Hudson, D. B.; Meleason, M. A.; Shoemaker, D. D. Int J Chem Kinet 1990, 20, 1051.
- Pritchard, G. O.; Follmer, D. W.; Meleason, M. A.; Shoemaker, D. D.; Perkins, J. C.; Leupp, S. J. Int J Chem Kinet 1992, 24, 735.
- Pritchard, G. O.; Johnson, K. A.; Nilsson, W. B. Int J Chem Kinet 1985, 17, 327.
- Pritchard, G. O.; Nilsson, W. B.; Marchant, P. E.; Case, L. C.; Parmer, J. F.; Youngs, R. F. Int J Chem Kinet 1984, 16, 69.
- Pritchard, G. O.; Abbas, S. H.; Piasecki, M. L.; Meleason, M. A. Int J Chem Kinet 1991, 23, 431.
- Georgakakos, J. H.; Rabinovitch, B. S.; Larson, C. W. Int J Chem Kinet 1971, 3, 535.