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Kinetics of the Photobromination of Fluoroethane. Estimate of the C–H Bond Dissociation Energies and the Heats of Formation of the CH_3CHF and CH_2CH_2F Radicals

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The gas-phase photobromination of fluoroethane was investigated in the temperature range 80—150 °C in both the presence and absence of chloroethane as an external competitor. The rate constant for α-hydrogen abstraction in CH_3CH_2F was redetermined relative to that in CH_3CH_2Cl, and the abstraction of β-hydrogen was measured in the internal competition. The relative rates were combined with the known rate parameters for the bromination of C_2H_6 to obtain the absolute rate constants ($cm^3\ mol^{-1}\ s^{-1}$): $k(\alpha) = (6.50\pm3.58)\times10^{12} \exp[-(10360\pm370)/RT]$ and $k(\beta) = (3.42\pm1.95)\times10^{12} \exp[-(12950\pm390)/RT]$.

Using a justifiable approximation concerning the magnitude of the activation-energy difference for the reverse reactions between any two competitors with similar complexity the following thermochemical quantities (kcal mol^{-1}) have been derived: $\Delta H^\circ{}_f(CH_3CHF) = -16.8\pm2$, $\Delta H^\circ{}_f(CH_2CH_2F) = -14.2\pm2$, $D^\circ(CH_3CHF\text{–}H) = 98.2\pm2$, $D^\circ(CH_2FCH_2\text{–}H) = 100.8\pm2$, and $D^\circ(CH_2CH_2\text{–}F) = 45.6\pm2$. The influence of halogen substitution on the rate parameters of hydrogen abstraction from monohaloethanes is discussed.

The thermochemical properties of halogenated hydrocarbons (HHCs) are now currently of interest in connection with understanding their behavior in the tropo- and stratosphere. The C–H bond dissociation energy, D°(R–H), is among the fundamental information indispensable to interpret the reactivity of organic compounds, and has been evaluated based on radical kinetics and mass spectrometry.[1)] From accumulated data concerning D°(R–H) of HHCs[2—4)] it is clear that the halogen substituents decrease D°(R–H) on the carbon of their substituted site, while their effect on D°(R–H) on the carbon of the adjacent sites remains unclear.[5,6)] Holmes and Lossing[7)] have recently evaluated $D^\circ(CH_3CHX\text{–}H)$ and $D^\circ(CH_2XCH_2\text{–}H)$, where X = Cl and Br, by monoenergy electron-impact spectroscopy, and concluded that the halogen substituents exert no effect on D°(R–H) on the adjacent site. Their findings were supported by a kinetic study on hydrogen abstraction by bromine atoms from CH_3CH_2Cl.[8)]

In the present study we extended our previous work[8,9)] by measuring the relative rates for α- and β-hydrogen abstraction from CH_3CH_2F in both the presence and absence of C_2H_5Cl as an external competitor. The rate parameters and the thermochemical quantities related to the CH_3CHF and CH_2FCH_2 radicals are reported.

Experimental

All of the chemicals, except for CH_3CHBrF, were obtained commercially: C_2H_5F and CH_2BrCH_2F from PCR; C_2H_5Cl, Tokyo Kasei; $CH_3CHBrCl$, Lancaster; and Br_2, Wako. Prior to their use, all samples were subjected to the usual trap-to-trap distillation and degassing under a vacuum at liquid-nitrogen temperature until the impurity levels were below the GC detection limit. The CH_3CHBrF needed for calibration was prepared by the bromination of C_2H_5F. A mixture of C_2H_5F (100 Torr, 1 Torr = 133.322 Pa) and Br_2 (50 Torr) was left standing at ambient temperature until the color of bromine disappeared; the compound was then isolated by means of preparative GC and purified as described above.

Kinetic experiments were carried out in a greaseless static system; the details concerning the experimental apparatus and procedure have been described elsewhere.[10)] The reaction temperatures ranged from 80 to 150 °C, and were maintained within 0.5 °C by circulating an ethylene glycol/water solution (approximately 4 : 1) through the outer jacket of a cylindrical Pyrex reactor. A highly pressurized halogen lamp was used as the light source, which directly irradiated the reactor without using a filter. The irradiation time was varied from 3 to 10 min for $C_2H_5F/C_2H_5Cl/Br_2$ and from 1 to 4 min for C_2H_5F/Br_2, depending on the reaction temperature, to keep the formation of undesirable secondary bromination products as low as possible. A product analysis was carried out using isothermal gas chromatography (180 °C for $C_2H_5F/C_2H_5Cl/Br_2$ with a flame-ionization detector and 150 °C for C_2H_5F/Br_2 with an electron-capture detector) and a Porapak 80/100 column of 2 m length. Calibration curves of the relative peak area vs. pressure for the products were determined by GC analyses of known amounts of the product gases diluted with nitrogen, yielding the following linear relationships: $S(CH_3CHBrF)/10^8 = (3.873\pm0.183)\times P(CH_3CHBrF) - (0.037\pm0.005)$, $(10^6 < S(CH_3CHBrF) < 2\times10^7, \mathrm{ECD})$; $S(CH_2BrCH_2F)/10^8 = (4.981\pm0.080)\times P(CH_2BrCH_2F)$, $(10^5 < S(CH_2BrCH_2F) < 10^6, \mathrm{ECD})$; $S(CH_3CHBrCl)/10^6 = (1.146\pm0.010)\times P(CH_3CHBrCl) - (0.022\pm0.007)$, $(10^5 < S(CH_3CHBrCl) < 10^7, \mathrm{FID})$; and $S(CH_3CHBrF)/10^6 = (1.064\pm0.012)\times P(CH_3CHBrF) -$

(0.016±0.005), ($10^5 < S(CH_3CHBrF) < 10^7$,FID). Here, S denotes the peak area (counts, range indicated in the parentheses) and P the pressure of the compounds (Torr).

Preliminary experiments confirmed the absence of dark reactions: when $C_2H_5F/C_2H_5Cl/Br_2$ (20 : 20 : 1) and C_2H_5F/Br_2 (20 : 1) mixtures were kept in a shield reactor for 30 min at 150 °C no products were found. The products observed under the present experimental conditions were $CH_3CHBrF/CH_3CHBrCl$ and CH_3CHBrF/CH_2BrCH_2F for respective mixtures; no secondary bromination products or ethylene arising from HX (X = F, Cl) elimination were detected.

Results and Discussion

Kinetics of Bromination of C_2H_5F. The kinetics of the gas-phase photo-bromination of C_2H_5F has been studied by both internal and external competition methods using C_2H_5Cl as an external reference, and related to C_2H_6 as a primary reference compound. The general scheme for competitive bromination has been reviewed;[10,11] the reactions of interest here are the following rate-determining propagation steps.

$$CH_3CH_2F + Br \rightarrow CH_2CH_2F + HBr \tag{1}$$

$$CH_3CH_2F + Br \rightarrow CH_3CHF + HBr \tag{2}$$

$$CH_3CH_2Cl + Br \rightarrow CH_3CHCl + HBr \tag{3}$$

$$C_2H_6 + Br \rightarrow C_2H_5 + HBr \tag{4}$$

For sufficiently long chains and low conversion <5% with respect to competitors, the reverse reaction may be neglected and the rate-constant ratios, without any noticeable error, are simply related to the measured product ratio:

$$k_1/k_2 = [CH_2BrCH_2F]/[CH_3CHBrF] \tag{5}$$

and

$$k_2/k_3 = [CH_3CHBrF][CH_3CH_2Cl]_0/[CH_3CHBrCl][CH_3CH_2F]_0, \tag{6}$$

where the subscript 0 denotes the initial concentration. The validity of Eqs. 5 and 6 was verified over a range of bromine pressure and photolysis time at a fixed competitor ratio. Thus, the relative rate, k_1/k_2, at 100.0 °C was independent of the irradiation time 2.0—4.5 min and the initial Br_2/C_2H_5F pressure ratio 10.5—31.5; k_2/k_3 at 100.0 °C was independent of the irradiation time 5.5—8.0 min and the initial $Br_2/C_2H_5Cl/C_2H_5F$ mixture pressure ratio 10.5—28.4 ($[C_2H_5Cl]_0/[C_2H_5F]_0 = 2.651$).

Figure 1 shows that the rate-constant ratio k_1/k_2 fits an Arrhenius rate law over the temperature range examined, and a least-squares analysis of the plot yields the expression

$$\ln(k_1/k_2) = -0.650 \pm 0.152 - (2590 \pm 120)/RT, \tag{7}$$

where R is in cal K^{-1} mol^{-1} and the stated uncertainties are one standard deviation. Whittle[12] et al. once reported k_2/k_4 based on the competitive bromination of C_2H_6 and C_2H_5F in the temperature range 40—120 °C as

$$\ln(k_2/k_4) = -2.111 \pm 0.080 + (1850 \pm 30)/RT.$$

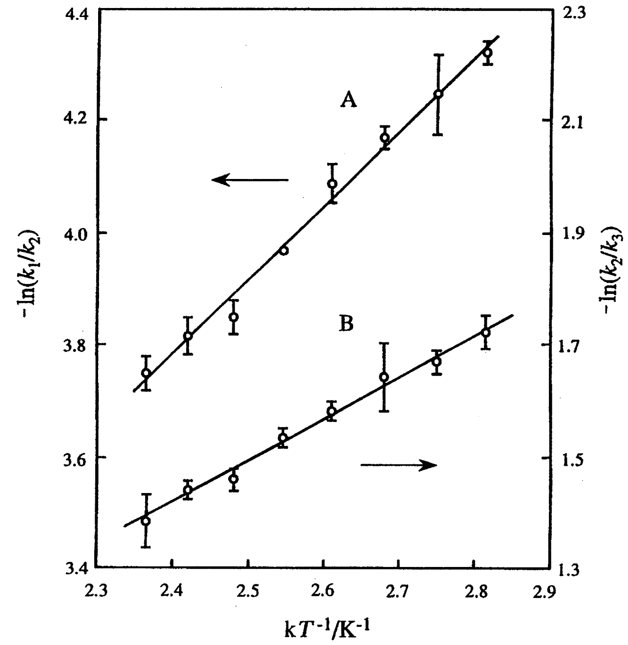

Fig. 1. Temperature dependence of (A) $k_1(CH_3CH_2F)/k_2(CH_3CH_2F)$ and (B) $k_2(CH_3CH_2F)/k_3(CH_3CH_2Cl)$.

Later, when they compiled the absolute rate parameters for H-abstraction from alkanes and haloalkanes by Br atoms, they revised their own value without any stated reason,[13] from which k_2/k_4 was calculated as

$$\ln(k_2/k_4) = -2.332 \pm 0.175 + (2070 \pm 220)/RT. \tag{8}$$

It thus seemed preferable to determine k_2/k_4 independently in this study. However, since a direct determination of k_2/k_4 was unsuccessful due to incomplete gas-chromatographic separation of the bromination products, C_2H_5Br and C_2H_4BrF, we chose C_2H_5Cl as a bridging compound to calculate k_2/k_4 from k_2/k_3 and k_3/k_4.

As shown in Fig. 1, k_2/k_3 determined from the competitive bromination of C_2H_5F and C_2H_5Cl in the temperature range 80—150 °C conforms with the Arrhenius rate law, and a least-squares analysis gave

$$\ln(k_2/k_3) = 0.289 \pm 0.062 - (1410 \pm 50)/RT. \tag{9}$$

The rate ratio k_3/k_4 has already been determined in the temperature range 70—150 °C as[8]

$$\ln(k_3/k_4) = -3.299 \pm 0.045 + (3710 \pm 30)/RT. \tag{10}$$

Combining Eqs. 9 and 10, we obtain

$$\ln(k_2/k_4) = -3.010 \pm 0.077 + (2300 \pm 60)/RT, \tag{11}$$

which agrees narrowly with Eq. 8 within the limits of the experimental error. We adopt Eq. 11 as k_2/k_4 in the following discussion.

Davies et al.[14] have determined k_4 directly over the temperature range 150—350 °C using the laser-flash photolysis of CF_2Br_2 as a source of Br atoms in the presence of C_2H_6, coupled with the time-resolved detection of $Br(^2P_{2/3})$ by resonance fluorescence:

$$k_4/\mathrm{cm^3\,mol^{-1}\,s^{-1}} = (1.32 \pm 0.72) \times 10^{14} \exp[(-12660 \pm 360)/RT]. \quad (12)$$

We adopt here these values as the standard with the tacit assumption that they are also valid at temperatures extending below 150 °C. Combining Eqs. 11 and 12 gives

$$k_2 = (6.50 \pm 3.58) \times 10^{12} \exp[-(10360 \pm 370)/RT], \quad (13)$$

and that of Eqs. 7 and 13 gives

$$k_1 = (3.42 \pm 1.95) \times 10^{12} \exp[-(12950 \pm 390)/RT]. \quad (14)$$

Table 1 gives the Arrhenius parameters for hydrogen abstraction by bromine atoms from CH_3CH_2X, X=H,[14] F, Cl,[8] and Br[15] along with the rate constants per equivalent hydrogen at 398 K, k_{398}, calculated from these parameters in order to compare the reactivity of the H-atoms in these compounds toward Br atoms. A comparison between k_{398} of ethane and those of haloethanes give some insight into the kinetic effect of the halogen substituents. The rate constants for a halogen-substituted site, $k_{398}(\alpha)$, are larger, while those for the adjacent site, $k_{398}(\beta)$, are smaller than that for ethane; i.e., upon H-abstraction a halogen substituent exerts an activating effect at an α-position and a deactivating effect at a β-position. The labilization of the α-hydrogen can be attributed to a decrease in the activation energies, which arises from inductive and resonance effects of the halogen atom and the ability of the methyl group to conjugate with the incipient tervalent carbon atom. A similar decrease in the activation energies by halogen substitution was also observed in CH_3X (X=H, F, Cl, and Br).[9,16] The delibilization of the β-hydrogen is somewhat surprising in view of the inductive effect of the halogen substituent; however, Tedder et al.[17,18] have observed such delibilization in the chlorination and bromination of fluorobutane and 1,1,1-trifluoropentane. As Table 1 shows, a change in pre-exponential factors accounts for the decrease in the $k_{398}(\beta)$ values, and the activation energies suffer little effect from halogen substitution. A small change in the activation energies could be interpreted as follows: the halomethyl group in β-haloethyl radicals can not conjugate with the tervalent carbon, which destabilizes the radicals compared with the ethyl radical. Such destabilization of the incipient radicals might cancel the activation of β-hydrogen due to an inductive effect of the halogen atoms. A decrease in the pre-exponential factors in both α- and β-H abstraction observed upon halogen substitution is qualitatively predictable on the basis of the linear three-atom activated-complex (BEBO) model[19] shown below. Provided that these compounds have a similar transition state,[15] i.e., similar n_1 and n_2, an increase in the mass of R causes a decrease in the pre-exponential factor.

$$\mathrm{RH + Br \rightarrow R \overset{n_1}{\cdots} H \overset{n_2}{\cdots} Br \rightarrow R + HBr} \qquad \begin{array}{l} \text{n: bond order} \\ n_1 + n_2 = 1 \end{array}$$

Thermochemical Quantities of Fluoroethane. Kinetic and equilibrium studies of bromination have been a major source of information concerning the free-radical heats of formation and bond-dissociation energies. From kinetic data alone, thermochemical data are preferably determined from a competitive reaction including a well known reference, since measurements of the relative rate constants and their temperature dependence are inherently more accurate than their absolute determination.

For any pair of bromination reactions,

$$\mathrm{RH + Br \underset{r}{\overset{f}{\rightleftarrows}} R + HBr} \quad \Delta H^\circ(T_\mathrm{m})$$

$$\mathrm{R'H + Br \underset{r}{\overset{f}{\rightleftarrows}} R' + HBr} \quad \Delta H^{\circ\prime}(T_\mathrm{m})$$

the difference in reaction enthalpies is given by

$$\begin{aligned} \Delta H^\circ(T_\mathrm{m}) - \Delta H^{\circ\prime}(T_\mathrm{m}) &= \Delta H_\mathrm{f}^\circ(\mathrm{R}) - \Delta H_\mathrm{f}^\circ(\mathrm{RH}) + \Delta H_\mathrm{f}^\circ(\mathrm{R'H}) - \Delta H_\mathrm{f}^\circ(\mathrm{R'}) \\ &= D^\circ(\mathrm{R{-}H}) - D^\circ(\mathrm{R'{-}H}) \qquad (15) \\ &= (E_\mathrm{f} - E_\mathrm{f}') - (E_\mathrm{r} - E_\mathrm{r}'), \qquad (16) \end{aligned}$$

where Eq. 16 is written in terms of the activation energies for the forward and reverse reactions and T_m denotes the mean temperature range over which the activation energies are measured. An evaluation of the heats of formation or the bond-dissociation energies at 298 K requires heat-capacity data which are not available for the fluoroethyl radicals. However, the heat-capacity corrections are usually quite small (e.g. for CF_3, the $\Delta H^\circ{}_\mathrm{f}$ values at 298 and 400 K differ by only 0.12 $\mathrm{kcal\,mol^{-1}}$) and are therefore neglected here.

The activation energies for the reverse reactions are difficult to measure, but have been considered to be small. Traditionally, the E_r values have been assumed to be on the order of $2 \pm 1\ \mathrm{kcal\,mol^{-1}}$ for any radical R.[1,3] Most recently, however, several investigators[20–24] and particularly Gutman and co-workers[22–24] have reported directly measured rate constants for the reactions of a series of alkyl radicals and HBr with the unexpected finding of small, but negative, temperature coefficients. For alkyl radicals the reported activation energies fall in a narrow range: -0.13 to $-1.39\ \mathrm{kcal\,mol^{-1}}$. In any case, since there is no direct determination of the E_r for the present compounds we must introduce an assumption concerning the magnitude of the E_r values in order to evaluate the thermochemical quantities of the present compounds. What is clear from the work of Gutman and co-workers as well as earlier studies[25,26] is that the absolute magnitude of E_r is generally small, and hence the difference $|E_\mathrm{r} - E_\mathrm{r}'|$ is generally small. Therefore, it is not unreasonable, as a first approximation, to assign the value $(E_\mathrm{r} - E_\mathrm{r}') = 0 \pm 1\ \mathrm{kcal\,mol^{-1}}$ for compounds of a similar type. With this assumption Eqs. 15 and 16 reduce to

$$D^\circ(\mathrm{R{-}H}) = D^\circ(\mathrm{R'{-}H}) + (E_\mathrm{f} - E_\mathrm{f}') - (0 \pm 1)\ \mathrm{kcal\,mol^{-1}}.$$

For evaluating $D^\circ(CH_3CHF{-}H)$ and $D^\circ(CH_2FCH_2{-}H)$ we choose C_2H_6 as a reference compound, since its E_f and E_r have been determined separately. From the thermochemical quantities $\Delta H^\circ{}_{\mathrm{f},298}(C_2H_6)$[27]$= -20.03 \pm 0.10$,

Table 1. Kinetic and Thermochemical Data of Ethane, Monohaloethanes, and Their Radicals[a]

RH	$\log A$	E_f	Ref.	$k_{398}/10^6$ [b]	$\Delta H^\circ_f(R)$	$D^\circ(R\text{–}H)$	$D^\circ(CH_2CH_2\text{–}X)$
CH_3CH_3	14.12 ± 0.24	12.66 ± 0.36	14	2.45(1)	28.36 ± 0.40[d]	100.5 ± 0.4	
$CH_3C\underline{H}_2F$	12.81 ± 0.25	10.36 ± 0.37	c)	6.60(2.69)	-16.8 ± 2	98.2 ± 2	
	13.10 ± 0.24	10.59 ± 0.37	13				
$C\underline{H}_3CH_2F$	12.53 ± 0.26	12.95 ± 0.39	c)	0.087(0.036)	-14.2 ± 2	100.8 ± 2	45.6 ± 2
$CH_3C\underline{H}_2Cl$	12.69 ± 0.24	8.95 ± 0.36	8	29.8(12.2)	17.9 ± 2	96.8 ± 2	
					19.3 ± 2[e]	98.2 ± 2[e]	
$C\underline{H}_3CH_2Cl$	12.58 ± 0.24	13.14 ± 0.36	8	0.077(0.0314)	22.0 ± 2	101.0 ± 2	19.4 ± 2
					22.8 ± 2[e]	101.7 ± 2[e]	
$CH_3C\underline{H}_2Br$	13.16 ± 0.25	10.40 ± 0.37	15	14.1(5.73)	31.3 ± 2	98.2 ± 2	
					27.3 ± 2[e]	94.2 ± 2[e]	
$C\underline{H}_3CH_2Br$					32.3 ± 2[e]	99.2 ± 2[e]	6.9 ± 2

a) Units: Pre-exponential (A) factors and k_{398} in $cm^3\ mol^{-1}\ s^{-1}$; all other quantities in $kcal\ mol^{-1}$. b) k_{398}=Rate constant at 398 K per equivalent hydrogen. Relative rate against ethane is given in the parentheses. c) This work. d) Ref. 29. e) Ref. 7.

$\Delta H^\circ{}_{f,298}(C_2H_5F)$[28]$=-62.9\pm0.4$, and $\Delta H^\circ{}_{f,298}(C_2H_5)$[29]$=28.36\pm0.40$ kcal mol^{-1} (collected from an appropriate reference), we obtain $\Delta H^\circ{}_{f,298}(CH_3CHF)=-16.8\pm2$ kcal mol^{-1} and $\Delta H^\circ{}_{f,298}(CH_2FCH_2)=-14.2\pm2$ kcal mol^{-1}, where the uncertainties are conservative estimates. Although experimental data comparable with the present results have not been published, Chen et al. have reported on an ab initio calculation of $\Delta H^\circ{}_{f,298}(CH_3CHF)=-17.3$[30] and $\Delta H^\circ{}_{f,298}(CH_2FCH_2)=-10.7$ kcal mol^{-1} [31] from iso-homodesmic reactions. The former value agrees well with the present estimate while the latter one differs considerably from the estimate. Although it is hard to assess what could cause such a large difference, it should be noted that the theoretical value leads to an E_r value for the CH_2FCH_2 radical of around -3.8 kcal mol^{-1}, which seems to contradict the findings by Gutman and co-workers described above.

Table 1 summarizes the C–H bond dissociation energies of ethane and monohaloethanes estimated from bromination kinetics (BK), along with those determined by the monoenergitic electron-impact (MEI) method.[7] The $D^\circ(CH_3CHCl\text{–}H)$, $D^\circ(CH_3CHBr\text{–}H)$, and $D^\circ(CH_2ClCH_2\text{–}H)$ from BK were revised upward by ca. 0.5 kcal mol^{-1} from the original estimates[8,15] based on the present assumption concerning the magnitude of the E_r values. Both $D^\circ(CH_3CHCl\text{–}H)$ and $D^\circ(CH_2ClCH_2\text{–}H)$ from two different methods agree well with each other, while $D^\circ(CH_3CHBr\text{–}H)$, determined by MEI method, considerably differs from that estimated from BK; it seems unrealistically small in view of the magnitude of the E_r value (calculated to be ca. 3 kcal mol^{-1}) for the H-abstraction reaction by bromine atoms. Although the $D^\circ(R\text{–}H)$ values from BK are associated with large uncertainties originating from the estimation of E_r, the representative $D^\circ(CH_3CHX\text{–}H)$ values decrease in the order H>Cl>Br≅F, being in accordance with the observed in $D^\circ(CH_2X\text{–}H)$.[16]

As for β-hydrogen $D^\circ(CH_2XCH_2\text{–}H)$, X=H, F, and Cl from BK fall in a narrow range around 100.5 kcal mol^{-1}, as expected from a small change in the E_f values upon halogen substitution. $D^\circ(CH_2BrCH_2\text{–}H)$ from an MEI measurement is somewhat lower (about 1 kcal mol^{-1}) than those of the ethane and the remaining ethanes from BK measurements.

For the 2-fluoroethyl radical, the bond-dissociation energy $D^\circ(CH_2CH_2\text{–}F)=45.6\pm2$ kcal mol^{-1} is calculated from the heat of the following reaction:

$$CH_2XCH_2 \rightarrow C_2H_4 + X.$$

The data required for the above calculation, $\Delta H^\circ{}_{f,298}(CH_2CH_2)$[27]$=12.5\pm0.1$ kcal mol^{-1} and $\Delta H^\circ{}_{f,298}(F)$[32]$=18.9\pm0.4$ kcal mol^{-1} were collected from an appropriate reference. The $D^\circ(CH_2CH_2\text{–}F)$ is fairly larger than $D^\circ(CH_2CH_2\text{–}Cl)=19.4\pm2$ and $D^\circ(CH_2CH_2\text{–}Br)=6.9\pm2$ kcal mol^{-1}, indicating that CH_2CH_2F radical is most stable for halogen elimination in these radicals. The formation of ethylene was observed in only the bromination of CH_3CH_2Br.[15]

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