ξ_2 and the reaction coordinate are the same order (see Figures 7 and 8), which further convinces one of the elliptical orbital of the hydrogen-bonded proton of malonaldehyde.

Of course, the result in this paper fairly depends on the accuracy of the calculated potential energy surface. It is well known that the CNDO/2 method reproduces the bond length, bond angle, and hydrogen bond energy well. The overestimate of the C–H stretching frequencies does not affect the results, since the change of frequencies along the reaction coordinate is sufficiently small. The complete geometry optimization and the normal coordinate calculation are of advantage in the present work. It should be noted that an arbitrary displacement of out-of-plane coordinate does not lower the potential energy,[8] whereas only one of six vibrational coordinates has a negative force constant on the reaction coordinate.

Compared with the microwave spectra, the calculated potential barrier along the reaction coordinate may be underestimated. Nevertheless, we believe that the essential result obtained in the present paper will not be altered by the use of a more reliable potential surface.

The method proposed in the present paper is also applicable to any type of unimolecular reaction. The dynamic nature or the rate of unimolecular reaction is under development at the present. These works are in progress and will be presented in the near future, so this paper will be regarded as a preliminary of this series.

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$$\sum_{K} \exp(-E_{Kn}/\kappa T) \Big/ \sum_{K} \sum_{m \in K} \exp(-E_{Km}/\kappa T)$$

The Kinetics and Thermochemistry of the Reaction of 1,1-Difluoroethane with Iodine. The CF_2–H Bond Dissociation Energy in 1,1-Difluoroethane and the Heat of Formation of 1,1-Difluoroethyl

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Abstract: The kinetics of the gas phase reaction of 1,1-difluoroethane with iodine have been determined over the temperature range 609 to 649 K. It was found that the initial stoichiometry was consistent with the reaction $CH_3CF_2H + I_2 \rightleftarrows CH_3CF_2I + HI$ but true equilibrium for this reaction was not obtained due to HI elimination from CH_3CF_2I which resulted in CH_3CF_2I reaching a steady state concentration at about 80 to 90% of its equilibrium value. However, kinetic data for the forward reaction obtained in the initial stages of reaction and at steady state were combined with previous results for the reverse reaction[1] to yield equilibrium constants over this temperature range from which $\Delta H_r°(298) = 12.2 \pm 0.2$ kcal/mol was obtained and $DH°(CH_3CF_2\text{–}H) = 99.5 \pm 1$ and $\Delta H_f°(CH_3CF_2,g,298) = -72.3 \pm 2$ kcal/mol were derived. A comparison of the effects of α and β fluorine substituents on the $C(sp^3)$–X (X = H, I, and F) bond dissociation energies is made.

As a part of a continuing study of the effect of fluorine on bond dissociation energies, we have recently reported on the kinetics of the gas phase reaction of 1,1-difluoroiodoethane with hydrogen iodide from which we derived $DH°(CH_3CF_2\text{–}I) = 52.1 \pm 1$ kcal/mol.[1] In this study, we wish to report the kinetics and thermochemistry of the reverse reaction, namely, 1,1-difluoroethane with iodine, from which we derive values for the CF_2–H bond dissociation energy, $DH°(CH_3CF_2\text{–}H)$, and the enthalpy of formation of 1,1-difluoroethyl, $\Delta H_f°(CH_3\dot{C}F_2,g,298)$. These are the first quantitative results on the effect of α fluorine substituents in ethanes and their comparison with previous results on the effects of β fluorine

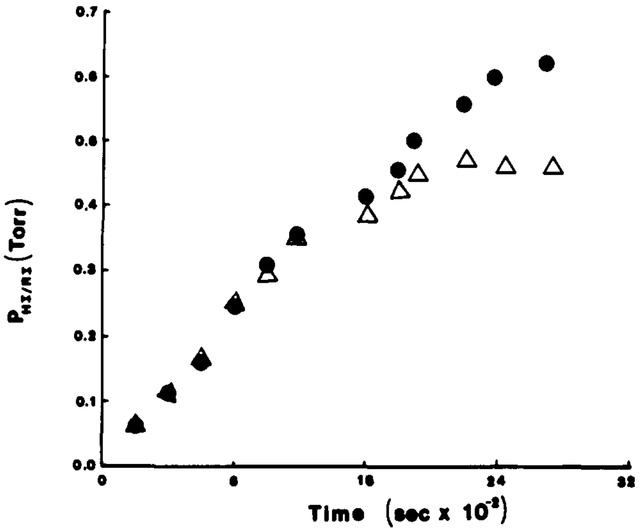

Figure 1. Stoichiometry at 609 K for the reaction of 1,1-difluoroethane with iodine: $P_{I_2}{}^{\circ}$ = 25.4 Torr, $P^{\circ}{}_{CH_3CF_2H}$ = 281 Torr; (△) $P_{CH_3CF_2I}$, measured at 270 nm; (●) P_{HI}, measured at 225 nm.

substituents indicates a surprising trend which, we feel, further emphasizes the importance of electrostatics in fluorine substitution.[2-4]

Experimental Section

Hydrogen iodide and 1,1-difluoroethylene were obtained from Matheson Gas Products, 1,1-difluoroethane from Union Carbide, and iodide from J. T. Baker Chemical Co. All were purified by vacuum distillation prior to use. The alkyl iodide 1,1-difluoroiodoethane was synthesized by conventional methods.[5]

The reaction was monitored spectrophotometrically using the apparatus previously described.[3] Before the first run at each temperature, the reaction cell was conditioned with a mixture of I_2, HI, and CH_3CF_2H in order to minimize the effects of surface. The absorption coefficients, α(OD $Torr^{-1}$), for HI, I_2, and CH_3CF_2I were determined at 225, 250, and 270 nm at each temperature. Since equilibrium lies far to the left, it was necessary to vary the pressure of CH_3CF_2H from 100 to 500 Torr in order to observe a measurable change in optical density. The iodine pressure was varied from 10 to 40 Torr.

Preliminary experiments at 270 nm showed a rapid increase in optical density in the initial stages of the reaction followed by a slow and continuous rise in both optical density and total pressure. The stoichiometry of the reaction was checked by following the appearance of HI and CH_3CF_2I at 225 and 270 nm. In these experiments, the pressure of CH_3CF_2I approached a constant value while the pressure of HI continuously increased. This was attributed to the unimolecular elimination of HI from CH_3CF_2I. Representative data are shown in Figure 1.

The thermal decomposition of CH_3CF_2H was also checked. In a conditioned reaction vessel, with 300 Torr of CH_3CF_2H no significant change in optical density or total pressure was observed for several hours.

As an equilibrium state could not be obtained, the thermochemistry was determined from kinetic considerations based on the rates of formation of HI and CH_3CF_2I at 250 and 270 nm as well as the rate of formation of HI at 225 nm after CH_3CF_2I had obtained a steady state.

At a particular wavelength, λ, the total absorbance is given by

$$A^{\lambda} = \sum_i \alpha_i{}^{\lambda} P_i \qquad \text{(i)}$$

where $\alpha_i{}^{\lambda}$ is the specific absorption coefficient of component i with a partial pressure, P_i. In the spectral region of 225 to 270 nm, $\alpha_{CH_3CF_2H}$ = 0.0, and under our experimental conditions, $\alpha_{I_2}\Delta P_{I_2}$ is negligible so that an apparent absorption coefficient for the reaction products may be expressed as

$$\alpha_{ap}{}^{\lambda} = \alpha_{HI}{}^{\lambda} + \alpha_{CH_3CF_2I}{}^{\lambda} \qquad \text{(ii)}$$

In the early stages of the reaction the stoichiometry is given by (see Figure 1)

$$-\Delta P_{I_2} = -\Delta P_{CH_3CF_2H} = \Delta P_{CH_3CF_2I} = \Delta P_{HI} \qquad \text{(iii)}$$

so that eq i and ii yield

$$\Delta A^{\lambda} = \alpha_{ap}{}^{\lambda} \Delta P_{CH_3CF_2I} \qquad \text{(iv)}$$

Thus, the rate of reaction becomes

$$\frac{dP_{HI}}{dt} = \frac{dP_{CH_3CF_2I}}{dt} = \Delta A^{\lambda}/(\alpha_{ap}{}^{\lambda}\Delta t) \qquad \text{(v)}$$

Later in the reaction, $dP_{CH_3CF_2I}/dt$ goes to zero and the rate of formation of HI then becomes

$$\left(\frac{dP_{HI}}{dt}\right)_{ss} = \Delta A^{\lambda}/(\alpha_{HI}{}^{\lambda}\Delta t) \qquad \text{(vi)}$$

The subscript "ss" refers to the fact that CH_3CF_2I is at a "steady state", i.e., $dP_{CH_3CF_2I}/dt \cong 0$.

Results

The stoichiometric relations of this reaction and the observation of Coomber and Whittle[6] that the bromination of 1,1-difluoroethane occurred exclusively (to within experimental accuracy) at the 1-carbon suggest the following mechanism

$$I_2 + M \rightleftharpoons 2I + M \qquad K_{I_2}$$

$$CH_3CF_2I + I \underset{2}{\overset{1}{\rightleftharpoons}} CH_3\dot{C}F_2 + I_2 \qquad (1,2)$$

$$CH_3\dot{C}F_2 + HI \underset{4}{\overset{3}{\rightleftharpoons}} CH_3CF_2H + I \qquad (3,4)$$

$$CH_3CF_2I \underset{6}{\overset{5}{\rightleftharpoons}} CH_2{=}CF_2 + HI \qquad (5,6)$$

for which the overall stoichiometry is

$$(1+\beta)CH_3CF_2H + (1+\beta)I_2 \rightleftharpoons CH_3CF_2I + \beta CH_2{=}CF_2 + (1+\beta)HI \qquad (7)$$

From the mechanism and the assumption that the free-radical concentrations are at steady state one obtains

$$\frac{d[HI]}{dt} = \frac{k_4K_{I_2}{}^{1/2}[RH][I_2]^{1/2}}{1 + (k_3[HI]/k_2[I_2])} \times \left[1 - \frac{[RI][HI]}{K_{eq}[RH][I_2]} + \frac{k_5[RI][HI]}{K_{eq}k_1K_{I_2}{}^{1/2}[RH][I_2]^{3/2}} + \frac{k_2k_5[RI]}{K_{eq}k_1k_3K_{I_2}{}^{1/2}[RH][I_2]^{1/2}}\right] \qquad \text{(vii)}$$

$$\frac{d[RI]}{dt} = \frac{k_4K_{I_2}{}^{1/2}[RH][I_2]^{1/2}}{1 + (k_3[HI]/k_2[I_2])} \times \left[1 - \frac{[RI][HI]}{K_{eq}[RH][I_2]} - \frac{k_5[RI][HI]}{K_{eq}k_1K_{I_2}{}^{1/2}[RH][I_2]^{3/2}} - \frac{k_2k_5[RI]}{K_{eq}k_1k_3K_{I_2}{}^{1/2}[RH][I_2]^{1/2}}\right] \qquad \text{(viii)}$$

In eq vii and viii[1]

$$K_{eq} = \frac{k_2k_4}{k_1k_3} = (10^{10.95-16.7/\theta})k_4$$

and, under our experimental conditions, namely, $P_{I_2}{}^0 \cong P_{I_2} \gg P_{HI}$ and $P_{RH}{}^0 = P_{RH}$, the second term in the brackets in eq vii and viii is negligible compared with the third term, so that these equations simplify to:

$$\frac{d[HI]}{dt} = k_4K_{I_2}{}^{1/2}[RH]_0[I_2]_0{}^{1/2}\left[1 - \frac{[RI][HI]}{K_{eq}[RH]_0[I_2]_0}\right.$$

Table I. Experimental Data and Equilibrium Constants for the Reaction $CH_3CF_2H + I_2 \rightleftarrows CH_3CF_2I + HI$ at 628 K

$P_{I_2}{}^0$, Torr	$P_{RH}{}^0$, Torr	Time, s	$\bar{D} \times 10^4$, Torr s^{-1}	P_{RI}, Torr	$(P_{RI})_{ss}$, Torr	$k_5 \times 10^4$, s^{-1}	$K_{eq} \times 10^{-5}$, Eq xii	Eq xiv[a]
29.9	324	400	7.00	0.50	0.60		4.5	4.4
19.2	326	300	7.45	0.30	0.43		4.0	3.5
16.9	342	300	7.35	0.36	0.51	4.9	4.8	5.2
10.2	332	600	3.17	0.30	0.35	4.6	4.1	4.3
36.1	210	500	4.24	0.44	0.60	2.2	4.2	5.7
16.5	240	700	2.74	0.33	0.39	3.7	4.1	4.6
12.5	525	400	7.06	0.43	0.50	4.3	4.7	4.3
11.6	226	400	4.18	0.20	0.30	3.7	4.2	4.2
21.8	220	600	3.87	0.30	0.40	3.2	3.7	4.1
16.0	374	500	4.63	0.40	0.50	4.2	4.2	4.8
					Av	3.9 ± 0.9	4.2 ± 0.3	4.5 ± 0.6

[a] Calculated using $\langle k_5 \rangle$.

$$+\frac{k_2k_5[\mathrm{RI}]}{K_{eq}k_1k_3K_{I_2}{}^{1/2}[\mathrm{RH}]_0[\mathrm{I}_2]_0{}^{1/2}}\Bigg] \quad \text{(ix)}$$

$$\frac{d[\mathrm{RI}]}{dt} = k_4K_{I_2}{}^{1/2}[\mathrm{RH}]_0[\mathrm{I}_2]_0{}^{1/2}$$

$$\times\Bigg[1 - \frac{[\mathrm{RI}][\mathrm{HI}]}{K_{eq}[\mathrm{RH}]_0[\mathrm{I}_2]_0} - \frac{k_2k_5[\mathrm{RI}]}{K_{eq}k_1k_3K_{I_2}{}^{1/2}[\mathrm{RH}]_0[\mathrm{I}_2]_0{}^{1/2}}\Bigg] \quad \text{(x)}$$

Adding eq ix and x yields

$$\tfrac{1}{2}\left(\frac{d[\mathrm{HI}]}{dt} + \frac{d[\mathrm{RI}]}{dt}\right) = \bar{D}$$

$$= k_4K_{I_2}{}^{1/2}[\mathrm{RH}]_0[\mathrm{I}_2]_0{}^{1/2}\left[1 - \frac{[\mathrm{RI}][\mathrm{HI}]}{K_{eq}[\mathrm{RH}]_0[\mathrm{I}_2]_0}\right] \quad \text{(xi)}$$

in which $\bar{D}$ is the average rate of formation of Hi and CH_3CF_2I (RI). The right-hand side of eq xi is the rate expression for the gas phase iodination of hydrocarbons in the absence of HI elimination.[7]

If we let $C = K_{I_2}{}^{1/2}k_1k_3/k_2 = 10^{12.58-34.4}$ $M^{-1/2}$ s^{-1}, then eq xi yields[1-8]

$$K_{eq} = \frac{\bar{D}}{C[\mathrm{RH}]_0[\mathrm{I}_2]_0{}^{1/2}} + \frac{[\mathrm{RI}][\mathrm{HI}]}{[\mathrm{RH}]_0[\mathrm{I}_2]_0} \quad \text{(xii)}$$

In the latter stages of the reaction $d(CH_3CF_2I)/dt = 0$ and $[CH_3CF_2I] = [RI]_{ss}$; during this steady state condition

$$\left[\frac{d[\mathrm{HI}]}{dt}\right]_{ss} = 2k_5[\mathrm{RI}]_{ss} \quad \text{(xiii)}$$

and

$$K_{eq} = \frac{[\mathrm{RI}]_{ss}[\mathrm{HI}]}{[\mathrm{RH}]_0[\mathrm{I}_2]_0} + \frac{k_5[\mathrm{RI}]_{ss}}{C[\mathrm{RH}]_0[\mathrm{I}_2]_0{}^{1/2}} \quad \text{(xiv)}$$

Equation xiii was used to obtain an average value for k_5 at each temperature and this was then used in eq xiv to determine K_{eq}. A summary of the experimental results at 628 K for eq xii, xiii, and xiv is given in Table I.

The partial pressures of CH_3CF_2I shown in Table I have a precision of ±10-20% and the equilibrium constants a precision of ±20-40%. Although these results have a large variance, free energy changes within ±0.5 kcal/mol can still be obtained and a similar precision is possible for the enthalpy of the reaction provided that the entropy change is known. The entropy change of this reaction is expected to be small and comparable to those of the series of reactions

$$CF_3CH_3 + I_2 \rightarrow CF_3CH_2I + HI \quad (8)$$

$$CH_3CH_3 + I_2 \rightarrow CH_3CH_2I + HI \quad (9)$$

$$CF_3H + I_2 \rightarrow CF_3I + HI \quad (10)$$

$$CH_4 + I_2 \rightarrow CH_3I + HI \quad (11)$$

for which the change in rotational symmetry between reactants and products is the predominant factor. Thus, the average intrinsic, or symmetry corrected, entropy change, $\Delta S_T{}^*$, for reactions 8 to 11 is given, within ±0.5 cal/K mol, by eq xv.[4,8-11]

$$\Delta S_T{}^* = -2.04 + 1.66 \ln (T/298) \quad \text{(xv)}$$

$$298 \le T \le 700 \text{ K}$$

The symmetry correction for reaction 7 ($\beta = 0$) is $R \ln 2$, and at a mean temperature of 625 K, eq xv yields

$$\Delta S_r{}^\circ(625) = 0.6 \text{ cal/K mol}$$

In addition, over the temperature range 700 to 300 K, $\Delta C_p{}^\circ = 2 \pm 0.5$ cal/K mol for reaction 7 ($\beta = 0$).[4,8-11]

Table II. Equilibrium Constants for the Reaction $CH_3CF_2H + I_2 \rightleftarrows CH_3CF_2I + HI$ between 609 and 649 K

Temp, K	$k_5 \times 10^4$, s^{-1}	Eq xii	$K_{eq} \times 10^5$, Eq xiv	Calcd
649	12.5 ± 5	5.0 ± 1.3	5.6 ± 1.7	6.1
628	3.9 ± 1	4.2 ± 0.3	4.5 ± 0.6	4.4
617	3.2 ± 1.5	4.0 ± 0.8	4.6 ± 1.6	3.6
609	3.0 ± 1	4.0 ± 0.9	3.0 ± 1.2	3.2

Equilibrium constants have been calculated from eq xii and eq xiii and xiv at four temperatures from data such as shown in Table I and they are summarized in Table II. The agreement between K_{eq} determined from the rate of reaction in its initial stages (eq xii) and those determined when $[CH_3CF_2I]$ has reached its steady state (essentially 80-90% of true equilibrium) is quite satisfactory and well within the experimental errors.

Using the entropy change calculated from eq xv for reaction 7 ($\beta = 0$) and the above estimate of the heat capacity change, one obtains

$$\log K_{eq} = 0.131 - 12.9/\theta$$

and

$$\Delta H_r{}^\circ(298 \text{ K}) = 12.2 \pm 0.2 \text{ kcal/mol}$$

This yields[8]

$$\Delta H_f{}^\circ(CH_3CF_2I,g,298) - \Delta H_f{}^\circ(CH_3CF_2H,g,298) = 20.8 \pm 0.2 \text{ kcal/mol}$$

Table III. Some Bond Dissociation Energies in Fluoroethanes

X	$DH°(CH_3CH_2-X)$, kcal/mol	$DH°(CH_3CF_2-X)$, kcal/mol	$DH°(CF_3CH_2-X)$, kcal/mol
H	98.0 ± 1[a]	99.5 ± 1[b]	106.7 ± 1[c]
I	53.4 ± 1[d]	52.1 ± 1[e]	56.3 ± 1[f]
F	107.5 ± 2[a,g]	124.8 ± 2[b]	109 ± 2[c,g]

[a] Reference 7. [b] This work. [c] Reference 4. [d] D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, **39**, 132 (1963). [e] Reference 1. [f] Reference 3. [g] Reference 10.

and

$$\Delta H_f°(CH_3CF_2I,g,298) = -98.9 \pm 1.5 \text{ kcal/mol}$$[10]

Discussion

The enthalpy change for reaction 7 ($\beta = 0$) may be expressed as

$$\Delta H_r°(298\text{ K}) = DH°(CH_3CF_2-H) + DH°(I-I) - DH°(CH_3CF_2-I) - DH°(H-I)$$

The values, $DH°(I-I) = 36.2$ kcal/mol and $DH°(H-I) = 71.3$ kcal/mol, are well known,[8] and from earlier work $DH°(CH_3CF_2-I) = 52.1 \pm 1$ kcal/mol,[1] so that the results of the present study yield

$$DH°(CH_3CF_2-H) = 99.5 \pm 1 \text{ kcal/mol}$$

In addition, our previous work[1] gave

$$k_1 = 10^{11.4-15.7/\theta}\ M^{-1}\ s^{-1}$$

and

$$k_2/k_3 = 10^{0.47+1/\theta}$$

so that the value of K_{eq} determined here yields

$$k_4 = 10^{11.0-29.6/\theta}\ M^{-1}\ s^{-1}$$

Terenishi and Benson[12] have studied the kinetics of the reaction

$$(CH_3)_3C-H + I \rightarrow (CH_3)_3C\cdot + HI \qquad (12)$$

and determined log (A_{12}, $M^{-1}\ s^{-1}$) = 10.8. Since isobutane is isoelectronic with CH_3CF_2H, the agreement with our result, log (A_4, $M^{-1}\ s^{-1}$) = 11.0, is satisfactory.

The heat of formation of the 1,1-difluoroethyl radical may be obtained by combining these results with $\Delta H_f°(H,g,298) = 52.1$ kcal/mol[8] and $\Delta H_f°(CH_3CF_2H,g,298) = -119.7 \pm 1.5$ kcal/mol[10] to yield

$$\Delta H_f°(CH_3\dot{C}F_2,g,298) = -72.3 \pm 1.8 \text{ kcal/mol}$$

This may, in turn, be combined with $\Delta H_f°(F,g,298) = 18.9$[8] and $\Delta H_f°(CH_3CF_3,g,298) = -178.2 \pm 0.4$ kcal/mol[10] to obtain

$$DH°(CH_3CF_2-F) = 124.8 \pm 2 \text{ kcal/mol}$$

Wu and Rodgers[13] have noted that $DH°(CF_3CF_2-X) - DH°(CH_3CH_2-X)$ is of the order of 2 ± 3 kcal/mol for X = H, Cl, Br, and I[14] but 19 kcal/mol for X = F! A similar trend was noted for $DH°(CF_3-X)$. The results of this work now show that two α fluorine substituents are sufficient to increase the $C(sp^3)-F$ bond dissociation energy 17 kcal/mol in substituted ethanes. Again, quite similar results have been obtained in the methanes, as $DH°(CHF_2-F) = 126 \pm 2$ kcal/mol.[15]

These results suggest that either the CF_3 moiety in RCF_3 compounds (R = H, CF_3, and CH_3) is unusually stable or the $R\dot{C}F_2$ radical is unusually unstable. However, the bond dissociation energy data for substituted ethanes summarized in Table III show that it is only the C-F bond that is so dramatically affected by two α fluorine substituents so that one is led to conclude that the CF_3 moiety must be unexpectedly stable. Just where the C-F bond dissociation energies in $RCHF_2$ compounds (or $RCXF_2$) will fall is a point of some interest and is currently under investigation.

Finally, the limited data of Table III show that the strengthening effect of three β fluorine substituents on the C-X bond energy decreases in the series X = H, I, and F. We have previously suggested that the increased value of the C-H bond dissociation energy in CF_3CH_3 could, in part, be due to changes in the electrostatic (or dipole-dipole) energy in the radical product and reactant.[4] In this vein, then, one would expect the attractive energy between the CF_3 and CH_2X moieties in CF_3CH_2X molecules to decrease in the order X = H, I, and F, and, since the radical product (CF_3CH_2) remains unchanged, the effect of three β fluorine substituents on the C-X bond energies should decrease in this order too. As may be seen by comparing columns 2 and 4 of Table III, this prediction is realized experimentally and lends further support to the importance of electrostatic effects in these compounds and free radicals.

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