Kinetics of the Gas Phase Reaction of Pentafluoroethyl Iodide with Hydrogen Iodide. Enthalpy of Formation of the Pentafluoroethyl Radical and the π Bond Dissociation Energy in Tetrafluoroethylene

E-Chung Wu and A. S. Rodgers*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received February 17, 1976*

Abstract: The kinetics of the gas phase reaction of pentafluoroethyl iodide with hydrogen iodide have been studied spectrophotometrically from 478 to 560 K. The rate-determining step was found to be $C_2F_5I + I \rightarrow \dot{C}_2F_5 + I_2$ for which $\log (k/\text{l. mol}^{-1}\ \text{s}^{-1}) = (11.2 \pm 0.3) - (16.8 \pm 0.8)/\theta$ ($\theta = 2.3RT$ in kcal/mol) was determined. This result was combined with established thermochemical data to yield the C–I bond dissociation energy, $DH°(CF_3CF_2\text{–}I) = 52.5 \pm 1$ kcal/mol, and the enthalpy of formation of pentafluoroethyl, $\Delta H_f°(CF_3\dot{C}F_2,g,298) = -213 \pm 1.3$ kcal/mol. This also led to an evaluation of the π bond dissociation energy in tetrafluoroethylene, $D\pi°(CF_2{=}CF_2) = 52.3 \pm 2$ kcal/mol. This value is shown to be in good agreement with the thermochemical data on tetrafluoroethylene.

In 1949, Lacher et al.[1] showed that the heat of addition of chlorine to tetrafluoroethylene was nearly 14 kcal/mol more exothermic than that to ethylene, and it has since been generally found that addition reactions to tetrafluoroethylene are more exothermic than those to ethylene.[2,3] This has been almost exclusively attributed to the destabilization of the C–C π bond by fluorine substitution,[4-6] though recently some evidence has been presented indicating that σ bond stabilization may be important too.[7]

In this paper, we wish to report on a kinetic study of the gas phase reaction of pentafluoroethyl iodide with hydrogen iodide, from which we derive the heat of formation of the pentafluoroethyl radical and, thereby, the π bond dissociation energy in tetrafluoroethylene.[8] We shall further show that this value of the π bond energy is in quantitative agreement with the thermochemical data for tetrafluoroethylene.

Experimental Section

Pentafluoroethyl iodide was obtained from the Pierce Chemical Co. and was vacuum distilled at dry ice temperatures before use. Gas-liquid chromatographic analysis on a 0.6 × 305 cm column packed with 30% dimethylsulfolane on Chromosorb W indicated that the sample, after distillation, was better than 99% pentafluoroethyl iodide. Hydrogen iodide, obtained from the Matheson Gas Co., was similarly distilled from a dry ice bath to a liquid N_2 trap and degassed at liquid N_2 temperatures before use. Iodine, obtained from the J. T. Baker Chemical Co., was sublimed in vacuo before use.

The kinetics of the reaction of C_2F_5I with HI were followed spectrophotometrically by observing the appearance of I_2 at 500 nm. The stoichiometry of the reaction was established from measurements at 225, 270, and 500 nm. Consequently, the absorption constants, $\alpha = \epsilon/RT$ in OD Torr^{-1}, were determined for C_2F_5I, HI, and I_2 at these wavelengths and at each reaction temperature.

The experimental apparatus and procedure has been described in detail previously and will not be repeated here.[9]

Results

The reaction of CF_3CF_2I with HI is expected to follow the well-established mechanism given by reactions 1 to 4.[10]

$$I_2 + M \rightleftarrows 2I + M \quad K_{I_2}$$

$$CF_3CF_2I + I \underset{2}{\overset{1}{\rightleftarrows}} CF_3\dot{C}F_2 + I_2 \qquad (1,2)$$

$$CF_3\dot{C}F_2 + HI \underset{4}{\overset{3}{\rightleftarrows}} CF_3CF_2H + I \qquad (3,4)$$

for which the overall reaction is:

$$CF_3CF_2I + HI \rightleftarrows CF_3CF_2H + I_2 \qquad (5)$$

The stoichiometry of this reaction was established at temperatures from 500 to 560 K by measuring the I_2 formed at 500 nm, the HI and CF_3CF_2I consumed at 225 and 270 nm, and the overall pressure change during the reaction at various reaction times. These data are summarized in Table I and, within experimental error, established reaction 5 as the only process taking place.

A steady-state treatment of the mechanism, neglecting reaction 4, gives

$$R_{I_2} = \frac{d(I_2)}{dt} = \frac{K_{I_2}^{1/2}k_1k_3[C_2F_5I][HI][I_2]^{1/2}}{k_2[I_2] + k_3[HI]} \qquad \text{(i)}$$

In order to obtain the rate constants k_1 and k_2/k_3, this equation was rearranged to

$$\frac{[HI]}{[I_2]} = k_1K_{I_2}^{1/2}\frac{[C_2F_5I][HI]}{[I_2]^{1/2}R_{I_2}} - \frac{k_2}{k_3} \qquad \text{(ii)}$$

Thus, a plot of $[HI]/[I_2]$ vs. $[RI][HI]/([I_2]^{1/2}R_{I_2})$ should give a straight line with slope equal to $k_1K_{I_2}^{1/2}$ and intercept equal to k_2/k_3. In each experiment, approximately 15 values of p_{I_2} (0.5 to 2.5 Torr) and time t were determined and p_{I_2} was fit by least squares to a fourth-order polynomial in time. The standard deviation of these fits was less than the estimated experimental error in p_{I_2}. This curve was then used to determine values of R_{I_2} and p_{I_2} at various times t and thus $[HI]/[I_2]$ and $[RI][HI]/[I_2]^{1/2}R_{I_2}$. The data for all experiments at a given temperature were then used to determine values of $k_1K_{I_2}^{1/2}$ and k_2/k_3 by a least-squares procedure. The results for four separate experiments at 477.7 K and the resulting least-squares line are shown in Figure 1. The values of k_1 and k_2/k_3 obtained by such plots at various temperatures are given in the fifth and sixth columns of Table II. The first three columns of this table give the temperature and the initial pressures (Torr) of HI and CF_3CF_2I for experiments at each temperature to show the pressure range and ratio of reactants used. The Arrhenius plot for k_1 is shown in Figure 2 and a least-squares analysis yields

$$\log (k_1/\text{l. mol}^{-1}\ \text{s}^{-1}) = (11.2 \pm 0.3) - (16.8 \pm 0.8)/\theta$$

The errors are one standard deviation, and $\theta = 2.303RT$ in kcal/mol. The logarithm of the A factor compares favorably

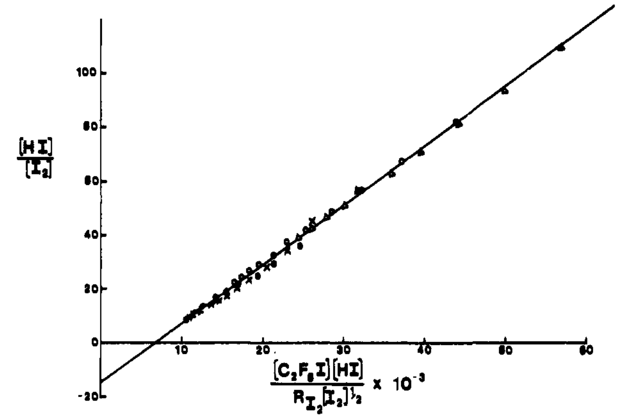

Figure 1. A plot of $[HI][I_2]^{-1}$ vs. $[C_2F_5I][HI][I_2]^{-1/2}$ rate^{-1} at 477.7 K. The initial conditions in Torr are: (△) HI = 63.5, C_2F_5I = 23.0; (○) HI = 39.1, C_2F_5I = 19.3; (X) HI = 21.7, C_2F_5I = 40.9; (●) HI = 20.1, C_2F_5I = 65.8.

Table I. Stoichiometric Study of the Reaction of CF_3CF_2I with HI at Various Temperatures

T, °K	Reaction time, min	ΔP_{I_2}, Torr	$-\Delta P_{HI}$, Torr	$-\Delta P_{C_2F_5I}$, Torr	ΔP_{total}, Torr
497	750	2.0	1.8	2.1	0.0
518	300	3.2	3.0	3.2	0.0
518	400	4.1	4.0	4.1	0.0
538	290	3.1	3.1	3.0	0.0
561	100	3.4	3.4	3.4	0.0
561	120	3.5	3.5	3.4	0.0
561	130	3.2	3.1	3.5	0.0

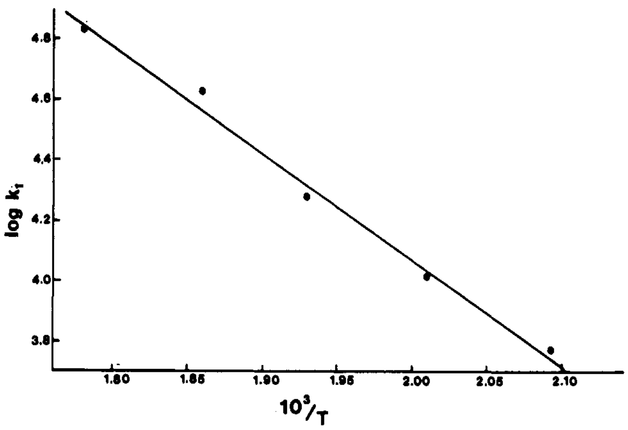

Figure 2. Arrhenius plot for the reaction $C_2F_5I + I \rightarrow C_2F_5 + I_2$.

with values reported for ethanes, namely 11.0 for C_2H_5I[10] and 11.5 for CF_3CH_2I.[9]

The values for k_2/k_3 are scattered; however, it has been repeatedly shown[10] that $E_3 - E_2 = 1.0 \pm 1$ kcal/mol and, assuming that is the case here, one obtains

$$\log (k_2/k_3) = (0.68 \pm 0.05) + (1.0 \pm 1)/\theta$$

Again, log (A_2/A_3) compares favorably with values previously determined. Namely, 0.60 for C_2H_5I[10] and 0.65 for CF_3CH_2I.[9]

Taken in conjunction with the assumption that $E_2 = 0.0 \pm 1$ kcal/mol,[10] the value for E_1 yields: $E_1 - E_2 = \Delta U_r°(1{,}518\text{K}) = \Delta H_r°(1{,}518\text{K}) = 16.8 \pm 1$ kcal/mol. Estimating[9] $\overline{\Delta C_{pr}°}(1) = -1 \pm .5$ cal K^{-1} mol^{-1}, from 518 to 298 K one then obtains:

$$\Delta H_f°(1{,}298) = 16.4 \pm 1 \text{ kcal/mol} \qquad \text{(iii)}$$

Discussion

(a) σ Bond Dissociation Energies. The C–I bond dissociation energy in CF_3CF_2I and the enthalpy of formation of pentafluoroethyl (CF_3CF_2) may be obtained by combining eq iii with $\Delta H_f°(CF_3CF_2I,g,298) = -240.0 \pm 1$ kcal/mol, determined previously by Wu, Pickard, and Rodgers,[3] $\Delta H_f°(I_2,g,298) = 14.9$ and $\Delta H_f°(I,g,298) = 25.5$ kcal/mol.[11] This yields:

$$DH°_{298}(CF_3CF_2\text{-}I) = 52.5 \pm 1 \text{ kcal/mol}$$

Table II. Kinetic Study of the Reaction $CF_3CF_2I + HI \rightarrow CF_3CF_2H + I_2$

T, °K	P(HI), Torr	$P(C_2F_5I)$, Torr	P_{I_2}, Torr	$k_1 \times 10^{-3}$, l. mol^{-1} s^{-1}	k_2/k_3
561.4	20.69	5.75	0.11		
	18.51	8.34	0.06		
	12.09	11.64	0.07		
	8.14	18.00	0.12		
	5.45	20.07	0.04	67.5 ± 2	10.4 ± 0.7
538.0	22.28	11.43	0.07		
	22.26	5.62	0.02		
	11.44	11.55	0.02		
	10.27	22.96	0.02		
	5.27	22.17	0.03	42.4 ± 1	15.0 ± 0.7
518.0	22.29	7.06	0.02		
	22.12	12.04	0.03		
	21.70	3.44	0.02		
	11.35	12.64	0.01		
	10.52	22.23	0.02		
	5.15	22.00	0.08	19.0 ± 0.3	11.0 ± 0.7
497.2	21.53	10.08	0.00		
	10.44	10.72	0.00		
	10.09	21.13	0.00	10.4 ± 0.2	13.3 ± 0.5
477.7	63.48	23.00	0.02		
	39.13	19.31	0.03		
	21.65	40.85	0.00		
	20.47	18.65	0.02		
	20.13	65.82	0.05	5.76 ± 0.03	14.8 ± 0.3

Table III. Bond Dissociation Energies for the C-X Bond in C_2F_5X and C_2H_5X

X	$DH°(CF_3CF_2\text{-}X)$, kcal/mol	$DH°(CH_3CH_2\text{-}X)$, kcal/mol
H	103.0 ± 1[a]	98.0 ± 1[b]
F	126.8 ± 1.3 (this work)	107.5 (est.)[c]
Cl	84.5 ± 1[d,e]	81.5 ± 1[f]
Br	68.3 ± 1[e,g]	67.7 ± 1[h]
I	52.5 ± 1.3 (this work)	53.4 ± 1[i]

[a] J. E. Bassett and E. Whittle, *J. Chem. Soc., Faraday Trans. 1*, **68**, 492 (1972). [b] Reference 10; this leads to $\Delta H_f°(CH_3\dot{C}H_2,g,298) = 25.7 \pm 1$ kcal/MOL/ [c] Reference 12 and footnote *b*. [d] J. W. Coomber and E. Whittle, *Trans. Faraday Soc.*, **63**, 2656 (1967). [e] W. G. F. Ford, Ph.D. Dissertation, Texas A&M University, May 1975. [f] J. Chao, A. S. Rodgers, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **3**, 141 (1974), and footnote *b*. [g] K. c. Ferguson and E. Whittle, *J. Chem. Soc., Faraday Trans. 1*, **68**, 306 (1972). [h] D. R. Stull, E. F. Westrum, and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969, and footnote *b*. [i] D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, **39**, 132 (1963).

and

$$\Delta H_f°(CF_3CF_2,g,298) = -213.0 \pm 1.3 \text{ kcal/mol}$$

This value and $\Delta H_f°(CF_3CF_3,g,298) = -320.9$,[12] $\Delta H_f°(CF_2{=}CF_2,g,298) = -157.4$, and $\Delta H_f°(F,g,298) = 18.9$ kcal/mol[11] lead to values for the C-F bond dissociation energy in hexafluoroethane and pentafluoroethyl, i.e., enthalpies of reactions 6 and 7:

$$CF_3CF_3 \rightarrow CF_3\dot{C}F_2 + F \qquad (6)$$

$$\dot{C}F_2CF_3 \rightarrow CF_2 = CF_2 + F \qquad (7)$$

thus, $DH°(CF_3CF_2\text{-}F) = \Delta H_r°(6) = 126.8 \pm 1.3$ and $DH°(\dot{C}F_2CF_2\text{-}F) = \Delta H_r°(7) = 74.5 \pm 1.3$ kcal/mol.

With these results, one can compare the values of the $C(sp^3)$-X bond dissociation energies in C_2F_5X with those in C_2H_5X for X = H, F, Cl, Br, and I. These data are summarized in Table III. The most outstanding feature of this table is that F for H substitution leaves the $C(sp^3)$-X bond nominally unchanged (2 ± 3 kcal/mol) with the striking exception of the C-F bond, which is strengthened by 20 kcal/mol!

The value of the $C(sp^3)$-F bond energy in ethyl fluoride is based upon an estimated enthalpy of formation,[12] but it is not reasonable to expect this estimate to be in error by 10 to 15 kcal/mol. In addition, a similar effect has been observed in CF_4 and CH_3F for which $DH°(CF_3\text{-}F) = 130.8 \pm 1$[13,14] and $DH°(CH_3\text{-}F) = 109.8 \pm 2$[10,13] kcal/mol. Thus, the 20 kcal/mol difference in the $C(sp^3)$-F bond dissociation energies on complete F for H substitution must be regarded as real. Consequently, an unexpected dichotomy exists in the effect of F for H substitution on the $C(sp^3)$-X bond energies. The explanation for this is at present unknown, but it has certainly stimulated our interest in further work on the effects of F for H substitution on bond energies.

(b) π Bond Dissociation Energies. The π bond dissociation energy of a monounsaturated compound has been defined as the difference in the bond dissociation energy of a given bond in the saturated compound and in the relevant free radical;[8] thus, for tetrafluoroethylene, $D\pi°(CF_2{=}CF_2) = \Delta H_r°(6) - \Delta H_r°(7) = 52.3 \pm 2$ kcal/mol.

This value is significantly less than the π bond dissociation energy in ethylene, $D\pi°(CH_2{=}CH_2) = 59.1 \pm 2$ kcal/mol,[8] but it is not sufficiently less (nominally 7 kcal/mol) so as to wholly account for the differences in the thermochemistry of addition reactions to ethylene and tetrafluoroethylene.[1-6]

The enthalpy of addition of a symmetric molecule X_2 to tetrafluoroethylene (reaction 8) may be expressed as eq iv.

$$X_2 + CF_2{=}CF_2 \rightarrow CF_2XCF_2X \qquad (8)$$

$$\Delta H_r°(8) = DH°(X\text{-}X) - DH°(CF_2XCF_2\text{-}X) - DH°(\dot{C}F_2CF_2\text{-}X) \qquad (iv)$$

However, the π bond dissociation energy for tetrafluoroethylene is given by:[8]

$$D\pi°(CF_2{=}CF_2) = DH°(CF_3CF_2\text{-}X) - DH°(\dot{C}F_2CF_2\text{-}X) \qquad (v)$$

so that substitution in eq iv yields:

$$\Delta H_r°(8) = DH°(X\text{-}X) + D\pi°(CF_2{=}CF_2) - DH°(CF_2XCF_2\text{-}X) - DH°(CF_3CF_2\text{-}X) \qquad (vi)$$

This may be simplified further if one makes the reasonable approximation that:

$$DH°(CF_2XCF_2\text{-}X) = DH°(CF_3CF_2\text{-}X)$$

so that eq vi becomes:

$$\Delta H_r°(8) = DH°(X\text{-}X) + D\pi°(CF_2{=}CF_2) - 2DH°(CF_3CF_2\text{-}X) \qquad (vii)$$

There are data on three different reactions of type 8, chlorination, bromination, and polymerization, for which quantitative comparison can be made.

(1) Chlorination. Lacher and co-workers[1] measured the heat of chlorination of tetrafluoroethylene calorimetrically and obtained $\Delta H_r°(8,Cl_2) = -57.3 \pm 0.2$ kcal/mol at 363 K, which may be corrected to $\Delta H_r°(8,Cl_2) = -57.4 \pm 0.2$ kcal/mol at 298 K. When one takes the value of $DH°(CF_3CF_2\text{-}Cl)$ from Table III and $DH°(Cl\text{-}Cl) = 58.2$ kcal/mol[11] then eq vii yields $\Delta H_r° = -58.5$ kcal/mol in good agreement with experiment.

(2) Bromination. The heat of bromination of tetrafluoroethylene was also determined calorimetrically by Lacher and co-workers[15] who obtained $\Delta H_r°(8,Br_2) = -38.7 \pm 1$ kcal/mol at 376 K which may be corrected to $\Delta H_r°(8,Br_2) = -38.8 \pm 1$ kcal/mol at 298 K. Again, eq vii, Table III, and $DH°(Br\text{-}Br) = 46.0$[11] yield $\Delta H_r°(8,Br_2) = -38.3$ kcal/mol in excellent agreement with experiment.

(3) Polymerization. For the polymerization of tetrafluoroethylene, X_2 becomes the gas phase polymer, $\text{-}(CF_2CF_2)_n\text{-}$, and $DH°(X\text{-}X)$ and $DH°(CF_2XCF_2\text{-}X)$ become identical; thus eq vi becomes:

$$\Delta H_{Poly}° = D\pi°(CF_2{=}CF_2) - DH°[CF_3CF_2\text{-}(CF_2CF_2)_n\text{-}] \qquad (viii)$$

No value for $DH°[CF_3CF_2\text{-}(CF_2CF_2)_n\text{-}]$ is known, but the gas phase heat of polymerization of tetrafluoroethylene has been estimated recently[7] at $\Delta H_{Poly}° = -37.2$ kcal/mol, so that eq viii results in:

$$DH°[CF_3CF_2\text{-}(CF_2CF_2)_n\text{-}] = 89.5 \text{ kcal/mol}$$

This is some 8 kcal/mol stronger than the estimate of the corresponding bond in polyethylene[8] and indicates considerable stabilization for the C-C σ bond.[7] This is not, however, an unexpected result in view of the fact that $DH°(CF_3\text{-}CF_3) = 98.7 \pm 1$ kcal/mol[12,14] while $DH°(CH_3\text{-}CH_3) = 88.4 \pm 1$ kcal/mol.[10]

Finally, it would be tempting at this time to conclude that F for H substitution destabilizes the π bond in ethylene, and such a view is further supported qualitatively by the rate parameters found by Jeffers[16] for the cis to trans isomerization of 1,2-difluoroethylene; however, we have just completed a determination of the π bond dissociation energy in 1,1-difluoroethylene[17] and obtained a value of $D\pi°(CH_2{=}CF_2) = 62.1$

kcal/mol which indicates that the interpretation of the fluorine substituent effect will not be a simple matter in π bonds either.

Acknowledgment. The authors gratefully acknowledge the support of this research by a Grant from the Robert A. Welch Foundation and one of us (E.C.W.) expresses his appreciation for a Robert A. Welch Postdoctoral Fellowship.

References and Notes

(1) J. R. Lacher, J. J. McKinley, C. M. Snow, L. Michel, G. Nelson, and J. D. Park, *J. Am. Chem. Soc.*, 71, 1330 (1949).
(2) C. R. Patrick, *Adv. Fluorine Chem.*, **2**, 1 (1961).
(3) E. C. Wu, J. M. Pickard, and A. S. Rodgers, *J. Phys. Chem.*, **79**, 1078 (1975).
(4) E. W. Schlag and E. W. Kaiser, Jr., *J. Am. Chem. Soc.*, **87**, 1171 (1965).
(5) J. P. Chesick, *J. Am. Chem. Soc.*, **88**, 4800 (1966).
(6) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).
(7) M. Ben-Yehuda, M. G. Katz, and L. A. Rajbenbach, *J. Chem. Soc., Faraday Trans. 1*, **70**, 908 (1974).
(8) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).
(9) E. C. Wu and A. S. Rodgers, *Int. J. Chem. Kinet.*, **5**, 1001 (1973).
(10) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).
(11) D. Stull, Ed., "JANAF Thermochemical Tables", The Dow Thermal Laboratory, Dow Chemical Co., Midland, Mich., U.S. Department of Commerce, PB No. 168370 and supplements.
(12) S. S. Chen, A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **4**, 441 (1975).
(13) A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **3**, 117 (1974).
(14) K. C. Ferguson and E. Whittle, *J. Chem. Soc., Faraday Trans. 1*, **68**, 295 (1972).
(15) J. R. Lacher, L. Casali, and J. D. Park, *J. Phys. Chem.*, **60**, 608 (1956).
(16) P. M. Jeffers, *J. Phys. Chem.*, **78**, 1469 (1974).
(17) J. M. Pickard and A. S. Rodgers, *J. Am. Chem. Soc.*, following paper in this issue.

Kinetics of the Gas Phase Addition of Bromine to 1,1-Difluoroethylene. π Bond Dissociation Energy of 1,1-Difluoroethylene

J. M. Pickard and A. S. Rodgers*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received February 17, 1976*

Abstract: The reaction of 1,1-difluoroethylene with bromine has been studied spectrophotometrically over the temperature range 550 to 620 K. The experimental results, based on initial rate measurements, are in good agreement with the following mechanism: $Br_2 \rightleftarrows 2Br$; $Br + CH_2{=}CF_2 \rightleftarrows CH_2BrCF_2\cdot$; $CH_2BrCF_2\cdot + Br_2 \rightleftarrows CH_2BrCF_2Br + Br$. A least-squares treatment of the data yields $\log k(\mathrm{l.}^{3/2}\ \mathrm{mol}^{-3/2}\ \mathrm{s}^{-1}) = (7.8 \pm 0.1) - (17.8 \pm 0.3)/\theta$, where θ equals $2.303RT$ kcal/mol. From the observed kinetic data, $DH°_{298}$ ($\cdot CF_2CH_2{-}Br$) was found to be 6.8 ± 1.0 kcal/mol. This value was combined with the known C–Br bond dissociation energy in CF_3CH_2Br to yield the π dissociation energy of 1,1-difluoroethylene as 62.1 ± 1.0 kcal/mol.

In the last several years, the influence of substituent effects on the rate of addition of free radicals to unsymmetrical fluoroethylenes has been the subject of several investigations. In particular, the rate of addition of H, CH_3, CF_3, and CF_2Br to 1,1-difluoroethylene has received considerable attention and the Arrhenius parameters are well characterized.[1-4] In the course of our investigations, we have found that radical addition reactions to olefins offer a pragmatic approach to measurement of π bond dissociation energies. In this study the analysis of the kinetics of the addition of bromine to 1,1-difluoroethylene is given and the implications regarding π bond dissociation energies are discussed.

Experimental Section

Anhydrous bromine from Mallinckrodt Chemicals was degassed and used without further purification. The 1,1-difluoroethylene from Matheson Gas Products was purified by bulb to bulb distillation from an *n*-pentane slush. Gas chromatographic analysis indicated that the purity was greater than 99% and the ir spectrum was identical with that previously reported.[5]

All kinetic runs were followed spectrophotometrically using an apparatus previously described.[6] The absorption coefficients of bromine, shown in Table I, were determined over the range 550 to 620 K at 440 nm. In a typical run, a known pressure of bromine was expanded into the reaction cell followed by that of 1,1-difluoroethylene. The bromine pressures were varied from 4 to 15 Torr while that of the olefin ranged from 12 to 250 Torr. The initial rate was determined as

$$-\mathrm{d}P/\mathrm{d}t = \Delta A/(\alpha \Delta t) \qquad \text{(i)}$$

where α is the absorption coefficient of bromine and ΔA is the change in bromine absorbance during a specific time interval, Δt. From this, the apparent rate constant was determined as

$$k_{\mathrm{ap}} = (\alpha^{-1}\,\Delta A/\Delta t)/(\bar{P}_{\mathrm{Br}_2})^{3/2}\,(\bar{P}_{\mathrm{CH_2{=}CF_2}}) \qquad \text{(ii)}$$

where $\bar{P}_{\mathrm{Br}_2}$ and $\bar{P}_{\mathrm{CH_2{=}CF_2}}$ are the average pressures within the interval Δt.

Results

The expected product of the reaction of bromine with 1,1-difluoroethylene would be 1,2-dibromo-1,1-difluoroethane. In kinetic runs with low conversion, nominally less than 50% of bromine, the total pressure change was equal to the total decrease in bromine. Gas chromatographic analysis of the quenched reaction mixture revealed only unreacted 1,1-difluoroethylene and one peak which had a retention time equivalent to an authentic sample of 1,2-dibromo-1,1-difluoroethane. Representative runs are tabulated in Table II. At large extents of reaction, measurable deviations occurred between the total pressure change and that of bromine; consequently, all data for the kinetic determinations were restricted to periods of time corresponding to the disappearance of less than 50% of the bromine.

The order of the reaction was determined from a plot of the logarithm of the initial rate vs. the logarithm of bromine and 1,1-difluoroethylene pressures. Order plots are shown in Figures 1 and 2 for bromine and 1,1-difluoroethylene, respectively. From the slopes of these plots, the reaction was found to be first order in olefin and $\frac{3}{2}$ order in bromine. Additional evidence