

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

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

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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: $\text{Br}_2 \rightleftharpoons 2\text{Br}$; $\text{Br} + \text{CH}_2=\text{CF}_2 \rightleftharpoons \text{CH}_2\text{BrCF}_2$; $\text{CH}_2\text{BrCF}_2 + \text{Br}_2 \rightleftharpoons \text{CH}_2\text{BrCF}_2\text{Br} + \text{Br}$. A least-squares treatment of the data yields $\log k(1.3^{1/2} \text{ mol}^{-3/2} \text{ s}^{-1}) = (7.8 \pm 0.1) - (17.8 \pm 0.3)/\theta$, where θ equals $2.303RT$ kcal/mol. From the observed kinetic data, $\text{DH}^\circ_{298}(\text{-CF}_2\text{CH}_2\text{-Br})$ was found to be 6.8 ± 1.0 kcal/mol. This value was combined with the known C-Br bond dissociation energy in $\text{CF}_3\text{CH}_2\text{Br}$ 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

$$-dP/dt = \Delta A/(\alpha \Delta t) \quad (\text{i})$$

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

$$k_{\text{ap}} = (\alpha^{-1} \Delta A/\Delta t)/(\bar{P}_{\text{Br}_2})^{3/2} (\bar{P}_{\text{CH}_2=\text{CF}_2}) \quad (\text{ii})$$

where \bar{P}_{Br_2} and $\bar{P}_{\text{CH}_2=\text{CF}_2}$ 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 $3/2$ order in bromine. Additional evidence

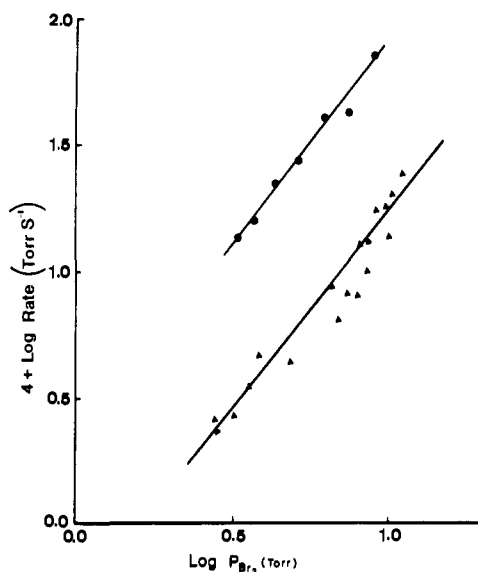


Figure 1. Variations of reaction rate with bromine pressure for the reaction $\text{CH}_2=\text{CF}_2 + \text{Br}_2 = \text{CH}_2\text{BrCF}_2\text{Br}$ at 554 K: (●) $\text{CH}_2=\text{CF}_2$ pressure 232.0 Torr; (▲) $\text{CH}_2=\text{CF}_2$ pressure 55.5 Torr.

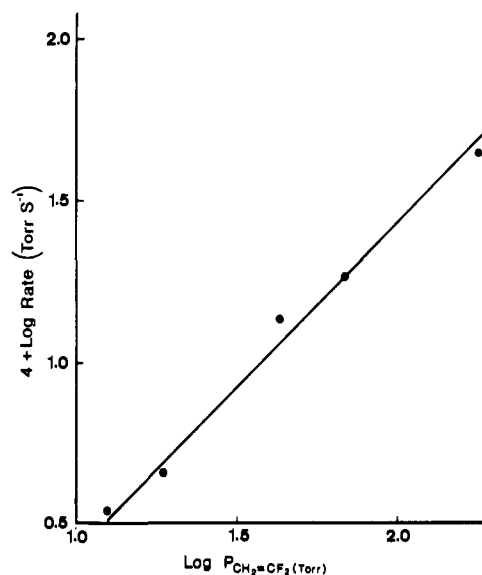


Figure 2. Variation of reaction rate with 1,1-difluoroethylene pressure for the reaction $\text{CH}_2=\text{CF}_2 + \text{Br}_2 = \text{CH}_2\text{BrCF}_2\text{Br}$ at 554 K; Br_2 pressure 8.9 Torr.

Table I. Apparent Absorption Coefficient for Bromine at λ 440 nm

Temp, °K	$\alpha,^a$ OD Torr ⁻¹	Temp, °K	$\alpha,^a$ OD Torr ⁻¹
620	0.0617	574	0.0691
604	0.0643	554	0.0722
581	0.0679		

^a Path length \approx 20 cm.

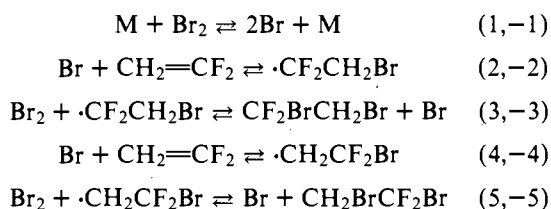
Table II. Stoichiometry of the Reaction $\text{CH}_2=\text{CF}_2 + \text{Br}_2 = \text{CH}_2\text{BrCF}_2\text{Br}$

Temp, °K	$P^\circ_{\text{Br}_2}$, Torr	$P^\circ_{\text{CH}_2=\text{CF}_2}$, Torr	ΔP_{Total} , Torr	$\Delta P_{\text{Br}_2},^a$ Torr
620	11.9	83.4	7.0	7.0
581	12.4	61.9	4.8	4.9
581	11.9	53.1	5.4	5.0
574	13.7	157.9	7.9	8.6

^a Determined spectrophotometrically at λ 440 nm.

for this reaction order comes from the consistent values of the apparent rate constant at 620 K shown in Table III.

The observed rate is consistent with the following mechanism:



From the steady state hypothesis, the assumption that k_{-2} and k_{-4} are greater than $k_3[\text{Br}_2]$ and $k_5[\text{Br}_2]$, respectively, and neglecting reactions -3 and -5 the following rate equation may be obtained:

Table III. Kinetic Data at 620 K for the Reaction $\text{CH}_2=\text{CF}_2 + \text{Br}_2 = \text{CH}_2\text{BrCF}_2\text{Br}$

$P^\circ_{\text{Br}_2}$, Torr	$P^\circ_{\text{CH}_2=\text{CF}_2}$, Torr	ΔP_{Br_2} , Torr	t , s	Rate, Torr s ⁻¹ $\times 10^{-2}$	K_{app} , M ^{-3/2} s ⁻¹
13.9	91.6	2.6	150	1.62	36.0
		4.0	250	1.29	36.0
		5.2	350	0.97	32.9
		6.1	450	0.89	36.0
11.9	83.1	1.1	90	1.48	38.4
		1.9	150	1.21	35.7
		2.6	210	1.21	40.3
		3.3	270	0.96	35.2
		3.8	330	0.95	39.3
		4.4	390	0.81	37.5
		4.8	450	0.68	34.5
		5.2	510	0.68	37.9
5.6	570	0.68	41.8		
					Av 37.8 \pm 2
13.9	34.9	3.1	300	0.55	37.7
		4.2	500	0.49	38.9
		5.1	700	0.41	38.6
		5.8	900	0.33	36.0
		6.5	1100	0.33	41.7
		7.0	1300	0.25	35.9
		7.5	1500	0.20	33.6
		7.9	1700	0.20	37.6
					Total av 37.2 \pm 2

$$\frac{-d[\text{Br}_2]}{dt} = k_3 \left(\frac{k_1}{k_{-1}} \right)^{1/2} \left(\frac{k_2}{k_{-2}} \right) \left[1 + \frac{k_5 k_4}{k_3 k_{-4}} \cdot \frac{k_{-2}}{k_2} \right] \times [\text{Br}_2]^{3/2} [\text{CH}_2=\text{CF}_2] \quad (\text{iii})$$

Since reactions 3 and 5 are exothermic abstractions from Br_2 , one expects $k_5/k_3 = 1$ so that $(k_4/k_{-4})(k_{-2}/k_2)$ will determine the "selectivity" of bromine atoms to $\text{CH}_2=\text{CF}_2$. Reactions 2 and 4 are exothermic bromine atom addition reactions and here too one expects $k_4/k_2 = 1$ so that "selectivity" now results from k_{-2}/k_{-4} . Here, we expect (-2) to be more endothermic than (-4), as $\text{DH}^\circ(\text{CF}_3\text{CH}_2\text{-Br}) > \text{DH}^\circ(\text{CH}_3\text{CF}_2\text{-Br})^8$ so

Table IV. Summary of Kinetic Data for the Reaction $\text{CH}_2=\text{CF}_2 + \text{Br}_2 = \text{CH}_2\text{BrCF}_2\text{Br}$

Temp, °K	No. of points/ No. of expt	Av rate const, $\text{M}^{-3/2} \text{s}^{-1}$
620	21/3	37.2 ± 2.4
604	54/8	24.4 ± 3.0
581	15/2	13.6 ± 1.0
574	81/10	12.5 ± 1.8
554	62/8	6.4 ± 1.1

that $k_{-2}/k_{-4} \leq 1$. This is consistent with other studies on $\text{CH}_2=\text{CF}_2$ which have shown that $\text{RCH}_2\dot{\text{C}}\text{F}_2$ is the principal radical species.^{2,4} Thus, eq iii becomes:

$$\frac{-d[\text{Br}_2]}{dt} \leq 2k_3 \left(\frac{k_1}{k_{-1}}\right)^{1/2} \left(\frac{k_2}{k_{-2}}\right) [\text{Br}_2]^{3/2} [\text{CH}_2=\text{CF}_2] \quad (\text{iv})$$

and

$$\frac{-d[\text{Br}_2]}{dt} \cong k_3 \left(\frac{k_1}{k_{-1}}\right)^{1/2} \left(\frac{k_2}{k_{-2}}\right) [\text{Br}_2]^{3/2} [\text{CH}_2=\text{CF}_2] \quad (\text{v})$$

In this study, the kinetic analyses were based on eq v. Note that if eq iv were applicable, the activation energy would remain essentially unchanged but the A factor would increase by a factor of 2. The data, such as that in Table III, were analyzed using eq v and the results at several temperatures are summarized in Table IV. An Arrhenius plot of these data is given in Figure 3 and a least-squares analysis resulted in:

$$\log(k_{\text{ap}}/\text{M}^{-3/2} \text{s}^{-1}) = (7.81 \pm 0.1) - (17.8 \pm 0.3)/\theta \quad (\text{vi})$$

In equation vi $k_{\text{ap}} = k_3(k_1/k_{-1})^{1/2}(k_2/k_{-2})$ and $\theta = 2.303RT$ kcal/mol.

From the thermodynamic data in the Appendix, one can obtain $(A_1/A_{-1})^{1/2}(A_2MA_{-2}) = 10^{-1.4} \text{M}^{-1/2} \text{s}^{-1}$ so that $A_3 = 10^{9.2 \pm 0.4} \text{M}^{-1} \text{s}^{-1}$. Reaction 3 is analogous to reaction 6; thus, the Arrhenius A factors should be comparable.



Whittle and co-workers⁷ have obtained $A_{-6} = 10^{11.3} \text{M}^{-1} \text{s}^{-1}$ from kinetic studies of bromination and this leads to $A_6 = 10^{8.9 \pm 0.4} \text{M}^{-1} \text{s}^{-1}$ when combined with data in Table V.

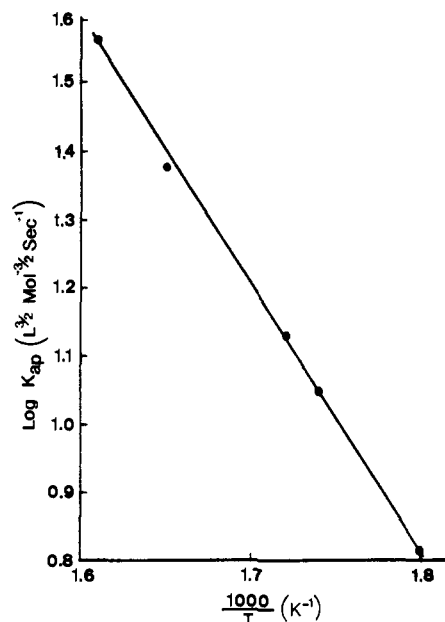
An alternative approach is to recognize that $K_{\text{eq}} = k_2k_3/(k_{-2}k_{-3})$ so that,

$$k_{\text{ap}} = k_{-3}K_{\text{eq}}(k_1/k_{-1})^{1/2} \cong k_{-6}K_{\text{eq}}(k_1/k_{-1})^{1/2} \quad (\text{vii})$$

The entropy of $\text{CF}_2\text{BrCH}_2\text{Br}$ may be estimated by group additivity⁹ from the data of Table V to yield $S^\circ(\text{CF}_2\text{BrCH}_2\text{Br}, \text{g}, 600\text{K}) \cong 106 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$, thus, $\Delta S_r^\circ(600\text{K})$ for the addition of Br_2 is approximately $-34.8 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$. Therefore, eq vii yields $A_{\text{ap}} = 10^{7.6} \text{M}^{-3/2} \text{s}^{-1}$. The good agreement between these two different ap-

Table V. Summary of Thermodynamic Data

Species	ΔH_f° , kcal/mol		S° , cal $\text{K}^{-1} \text{ mol}^{-1}$		C_p° , cal $\text{K}^{-1} \text{ mol}^{-1}$		Ref
	298 K	600 K	298 K	600 K	298 K	600 K	
Br_2	7.38	10.04	58.63	64.78	8.61	8.91	10
Br	26.73	28.22	41.80	45.27	4.97	4.99	10
$\text{CH}_2=\text{CF}_2$			63.38	75.79	14.14	21.32	16
$\text{CF}_3\text{CF}_2\text{Br}$			86.97	108.76	26.14	36.23	8
$\text{CF}_3\text{CH}_2\text{Br}$			80.63	99.27	21.57	31.61	8
CF_3CF_3			79.30	100.80	25.43	35.60	17

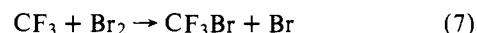
**Figure 3.** Arrhenius plot for the reaction $\text{CH}_2=\text{CF}_2 + \text{Br}_2 = \text{CH}_2\text{BrCF}_2\text{Br}$ from 554 to 620 K.

proaches and the experimental result adds further support to the proposed mechanism.

From eq v and vi, one sees that the apparent activation energy is given by:

$$E_{\text{ap}} = 0.5\Delta U^\circ_{1,-1} + \Delta U^\circ_{2,-2} + E_3 = 17.8 \pm 0.3 \text{ kcal/mol} \quad (\text{viii})$$

The quantity $\Delta U^\circ_{1,-1}$ is well known¹⁰ and E_3 is expected to be small. Whittle and co-workers⁷ have shown that $E_7 = 0.7 \pm 1 \text{ kcal/mol}$ so that



$E_3 = 0.7 \pm 1 \text{ kcal/mol}$ seems a reasonable estimate. Thus, from eq viii, $\Delta U^\circ(2, -2, 600\text{K}) = -5.6 \pm 1$ and $\Delta H^\circ(2, -2, 600\text{K}) = -6.8 \pm 1 \text{ kcal/mol}$. The average heat capacity difference ($\Delta \bar{C}_p^\circ$) from 600 to 300 K is nominally zero so that: $-\Delta H^\circ(2, -2, 298\text{K}) = \text{DH}^\circ_{298}(\dot{\text{C}}\text{F}_2\text{CH}_2-\text{Br}) = 6.8 \pm 1 \text{ kcal/mol}$.

The π bond dissociation energy for $\text{CH}_2=\text{CF}_2$ is defined as the difference in the bond dissociation energies for the same bond in both the saturated and relevant free radical species,¹¹ thus

$$D\pi^\circ(\text{CH}_2=\text{CF}_2) = \text{DH}^\circ(\text{CF}_3\text{CH}_2-\text{Br}) - \text{DH}^\circ(\dot{\text{C}}\text{F}_2\text{CH}_2-\text{Br}) \quad (\text{ix})$$

as well as

$$D\pi^\circ(\text{CH}_2=\text{CF}_2) = \text{DH}^\circ(\text{CH}_3\text{CF}_2-\text{Br}) - \text{DH}^\circ(\dot{\text{C}}\text{H}_2\text{CF}_2-\text{Br}) \quad (\text{x})$$

Ford⁸ has recently determined that $\text{DH}^\circ(\text{CF}_3\text{CH}_2-\text{Br}) = 68.9$

± 1 kcal/mol so that eq ix yields $D\pi^\circ(\text{CH}_2=\text{CF}_2) = 62.1 \pm 1.5$ kcal/mol.

Discussion

We have recently shown that the π bond dissociation energy of tetrafluoroethylene is 52.5 kcal/mol,¹² 7 kcal less than that for ethylene at 59 kcal/mol.¹¹ Thus, the value of 62.1 kcal/mol for the π bond dissociation energy of 1,1-difluoroethylene found in this work is unexpectedly strong, and neither fluorine substitution nor electronegativity per se can account for these data.

These data do suggest, however, that the difference in the electronegativity of the π bond centers may be the important factor. This suggestion is also indicated by the increased strength of the π bond in formaldehyde, which has been found to be 71 ± 2 kcal/mol,¹³ some 12 kcal stronger than ethylene. Certainly some of this increase results from the shorter π bonding distance in formaldehyde as opposed to ethylene but some of it may also result from the greater electronegativity of the O atom compared to CH_2 . This is further supported by the methyl substituent effect for both the C-C and C-O π bonds. Thus, in ethylene there is no difference in electronegativity of the π bonding centers so that methyl substitution, to give isobutylene, leaves the π bond essentially unchanged at 58 kcal/mol.¹¹ On the other hand, in formaldehyde, the difference in electronegativity of the two centers places an electron demand on the carbon center so that methyl substitution, to give acetone, increases the π bond energy by nearly 7 kcal to 77.5 kcal/mol.¹⁴

Thus, estimations of the effect of substituents upon π bond dissociation energies involve considerations of the effect of that substituent upon the difference in electronegativity of the π bonding centers.

Such considerations would predict that the π bond energy in difluorocarbonyl should be less than that in formaldehyde while that in hexafluoroacetone should be a great deal less than that in acetone. This latter effect could account, at least in part, for the much more stable hydrate of hexafluoroacetone (2,2-perfluoropropanediol) as opposed to that of acetone (2,2-propanediol).¹⁵

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Appendix

The thermodynamic data used in this work are summarized in Table V.

The thermodynamic properties of a free radical, for example, the entropy, have been approximated by

$$S^\circ(\dot{\text{R}}, \text{g}, T) = S^\circ(\text{RX}, \text{g}, T) + \Delta S_{\text{m}}^\circ + \Delta S_{\text{r}}^\circ + \Delta S_{\text{vib}}^\circ + \Delta S_{\text{ir}}^\circ + \Delta S_{\text{e}}^\circ + \Delta S_{\sigma}^\circ \quad (\text{xi})$$

Table VI. Calculated Values for the Product of the Moments of Inertia and Reduced Moments for Internal Rotation

Species	I_r , amu A ²	$I_a I_b I_c$, amu ³ A ⁶
$\text{CF}_3\text{CH}_2\text{Br}^a$	31.85	17.61×10^6
$\text{CH}_2\text{Br}\dot{\text{C}}\text{F}_2$	22.66	7.48×10^6
$\text{CF}_3\dot{\text{C}}\text{F}_3^b$	44.12	13.10×10^6
$\text{CF}_3\dot{\text{C}}\text{F}_2$	34.02	6.80×10^6

^a Reference 8. ^b Reference 17.

in which RX is a stable compound of the radical R· and the atom X and $\Delta S_{\text{m}}^\circ$, $\Delta S_{\text{r}}^\circ$, $\Delta S_{\text{vib}}^\circ$, $\Delta S_{\text{ir}}^\circ$, $\Delta S_{\text{e}}^\circ$, and ΔS_{σ}° represent corrections to the entropy of RX for changes in mass, overall rotation, vibration, internal rotation, electronic state, and symmetry, respectively, due to the loss of X to form the radical. For the radicals $\text{CH}_2\text{Br}\dot{\text{C}}\text{F}_2$ and $\text{CF}_3\dot{\text{C}}\text{F}_2$ the model compounds were CH_2BrCF_3 and C_2F_6 . The structure and barriers to internal rotation were assumed to remain unchanged with loss of one F atom and the results for the product of the principal moments and of the reduced moment for internal rotation are summarized in Table VI. The loss of a F atom was associated with a loss of a C-F stretching mode at 1200 cm^{-1} and two FCF bending modes at 600 and 350 cm^{-1} . The rotational symmetry numbers for $\text{CH}_2\text{Br}\dot{\text{C}}\text{F}_2$ and $\text{CF}_3\dot{\text{C}}\text{F}_2$ were 1 and 3, and electronic ground states were taken as doubly degenerate. On this basis, we obtain $S^\circ(\text{CH}_2\text{Br}\dot{\text{C}}\text{F}_2, \text{g}, 600\text{K}) = 97.0$ and $S^\circ(\text{CF}_3\dot{\text{C}}\text{F}_2, \text{g}, 600\text{K}) = 100.1\text{ cal K}^{-1}\text{ mol}^{-1}$.

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