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The Gas-Phase Kinetics of the Reaction of 1,1-Difluoroiodoethane with Hydrogen Iodide: The C–I Bond Dissociation Energy in 1,1-Difluoroiodoethane

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Abstract

The kinetics of gas-phase reaction of CH_3CF_2I with HI were studied from 496 to 549K and have been shown to be consistent with the following mechanism:

$$I_2 + M \rightleftarrows 2I + M$$

$$CH_3CF_2I + I \underset{2}{\overset{1}{\rightleftarrows}} CH_3\dot{C}F_2 + I_2 \tag{1,2}$$

$$CH_3\dot{C}F_2 + HI \underset{4}{\overset{3}{\rightleftarrows}} CH_3CF_2H + I \tag{3,4}$$

A least squares treatment of the data gave

$$\log k_1(M^{-1} \cdot \sec^{-1}) = (11.4 \pm 0.3) - \frac{(15.7 \pm 0.8)}{\theta}$$

where $\theta = 2.303\ RT$ kcal/mole. The observed activation energy E_1 was combined with $E_2 = 0 \pm 1$ kcal/mole to yield

$$DH^\circ(CH_3CF_2 - I) = 52.1 \pm 1.0 \text{ kcal/mole}$$

The result, combined with data for several C–I bond dissociation energies, leads us to conclude that the $C(sp^3)$–I bond is relatively insensitive to F for H substitution and that the $C(sp^2)$–I bond has considerable double-bond character.

Introduction

Extensive work by Benson and coworkers [1] has shown that the gas-phase reactions of hydrogen iodide with a wide variety of alkyl halides may be satisfactorily explained by the following mechanism:

$$I_2 + M \rightleftarrows 2I + M$$

(1,2) $$RI + I \underset{2}{\overset{1}{\rightleftarrows}} \dot{R} + I_2$$

(3,4) $$\dot{R} + HI \underset{4}{\overset{3}{\rightleftarrows}} RH + I$$

From the observed activation energy E_1, the known bond dissociation energy of iodine, and the reasonable assumption [2–6] that $E_2 = 0 \pm 1$ kcal/mole, values of $\Delta H_r^\circ(1,298K)$ may be determined from which accurate values of C–I bond dissociation energies are derived. More recently Wu and Rodgers [7,8a], investigating the influence of fluorine on sigma bond energies, reported the kinetics of the reactions of CF_3CH_2I and CF_3CF_2I with HI. In the present work we wish to report on the kinetics of the analogous reaction of CH_3CF_2I with HI and the resulting C–I bond dissociation energy.

Experimental

Hydrogen iodide from Matheson Gas Company was degassed and purified by vacuum distillation from an *n*-pentane slush. Reagent grade iodine from J. T. Baker Chemical Company was purified by sublimation prior to use. The alkyl iodide, 1,1-difluoroiodoethane [9], was synthesized by the addition of HI (0.04 mole) to 1,1-difluoroethylene (0.02 mole) in the liquid phase at 20°C. After complete reaction, excess HI was removed by absorption over ascarite and the sample was dried on a molecular sieve. Unreacted olefin was removed by distillation over glass beads at −70°C. Gas-chromatographic analysis on a 0.6 × 305-cm column packed with 30% dimethylsulfolane on Chromasorb W showed that the sample was greater than 98% 1,1-difluoroiodoethane. Sample identity was confirmed by ultraviolet ($\lambda_{max} = 270$ nm), gas-phase infrared [10], and liquid-phase Raman spectra.

All kinetic measurements were conducted with an apparatus previously described [7].

Prior to kinetic runs at each temperature, the absorption coefficients (OD torr^{-1}) of CH_3CF_2I, HI, and I_2 were determined from Beer's law plot of OD versus pressure at 225, 270, and 500 nm. In a typical run, HI was expanded into the reaction cell and the pressure was measured manometrically. This was followed by a quantity of CH_3CF_2I, and its pressure was determined by difference. Reaction rates were determined spectrophotometrically from the appearance of I_2 at 500 nm as a function of time. Independent measurements of the disappearance of HI and CH_3CF_2I at 225 and 270 nm were used to verify the stoichiometry of the reaction.

Results and Discussion

Application of the steady-state hypothesis to the assumed mechanism, neglecting reaction (4), yields the following rate expression:

$$R_{I_2} = \frac{d[I_2]}{dt} = \frac{k_1k_3K_{I_2}^{1/2}[RI][HI][I_2]^{1/2}}{k_2[I_2] + k_3[HI]} \tag{I}$$

Equation (I) was rearranged to

$$\frac{[HI]}{[I_2]} = \frac{k_1K_{I_2}^{1/2}[RI][HI]}{R_{I_2}[I_2]^{1/2}} - \frac{k_2}{k_3} \tag{II}$$

Thus a plot of $[HI]/[I_2]$ versus $[RI][HI]/R_{I_2}[I_2]^{1/2}$ should yield a straight line with slope $k_1K_{I_2}^{1/2}$ and intercept $-k_2/k_3$. The rate of formation of I_2, R_{I_2}, was determined by differentiation of a fourth-order polynomial fit of P_{I_2} versus time. A plot of eq. (II) at 496K is shown in Figure 1 for a tenfold variation in the ratio of $[HI]/[I_2]$. The initial pressures of HI and CH_3CF_2I, the observed rate constants for each run, and the total number of experimental points for each temperature in the range of 496–549K are summarized in Table I.

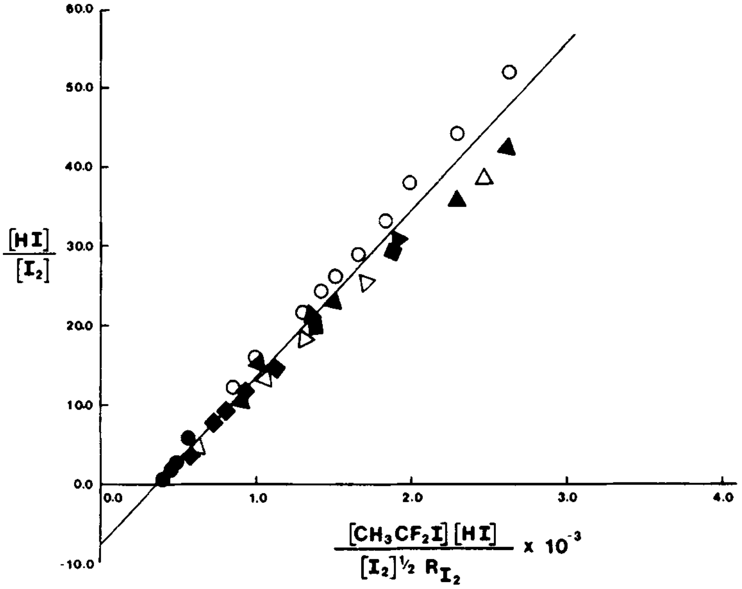

Figure 1. Kinetic plot at 496K for the reaction $CH_3CF_2I + I \rightarrow CH_3\dot{C}F_2 + I_2$. The initial pressures, in torr, are: ○—HI = 35.0, CH_3CF_2I = 6.9; ▲—HI = 19.6, CH_3CF_2I = 2.6; △—HI = 13.0, CH_3CF_2I = 5.2; ■—HI = 11.5, CH_3CF_2I = 8.2; ●—HI = 3.1, CH_3CF_2I = 10.6. Essentially every other data point in each of the five experiments was deleted for clarity. Solid line—least squares fit for all 82 data points.

TABLE I. Summary of the kinetic data for the reaction of 1,1-difluoroiodoethane with hydrogen iodide.

TEMP K	$P°(HI)$ Torr	$P°(CH_3CF_2I)$ Torr	$k_1 \times 10^{-3}$ $M^{-1}s^{-1}$	$\frac{k_2}{k_3}$	# of points
496	34.99	6.86			
	19.58	2.58			
	12.97	5.20			
	11.48	8.19			
	3.11	10.57			
	2.10	20.00	27.3 ± 0.5	7.4 ± 0.5	82
511	31.62	2.66			
	25.34	3.29			
	21.14	12.78			
	19.75	2.12			
	13.48	7.39	43.1 ± 0.6	7.5 ± 0.7	88
521	22.62	2.11			
	11.43	4.90			
	5.13	5.69			
	2.49	22.47	56.3 ± 0.5	9.5 ± 0.2	66
535	21.57	3.18			
	15.80	4.67			
	15.36	1.64			
	10.37	5.33	81.7 ± 0.7	6.2 ± 0.3	104
549	21.04	3.02			
	10.16	5.07			
	9.96	5.91			
	5.63	5.58	134.0 ± 1.9	6.7 ± 0.3	93

TABLE II. Stoichiometric study at 496K for the reaction: $CH_3CF_2I + HI \rightarrow CH_3CF_2H + I_2$.

P°_{HI} Torr	$P^\circ_{CH_3CF_2I}$	Time sec	$-\Delta P_{HI}$	$-\Delta P_{CH_3CF_2I}$	ΔP_{I_2}
11.49	8.19	4640	2.0	1.7	2.1
		6100	2.5	2.2	2.6
3.11	10.57	6480	1.3	1.2	1.6
12.98	5.20	9420	2.5	2.1	2.5
19.58	2.58	20500	2.1	1.8	–

The stoichiometry of the reaction was verified by monitoring the appearance of I_2 at 500 nm and the disappearance of HI and CH_3CF_2I at 225 and 270 nm in several experiments. In each experiment the total pressure change was negligible and the good agreement between the pressure changes of I_2, HI, and

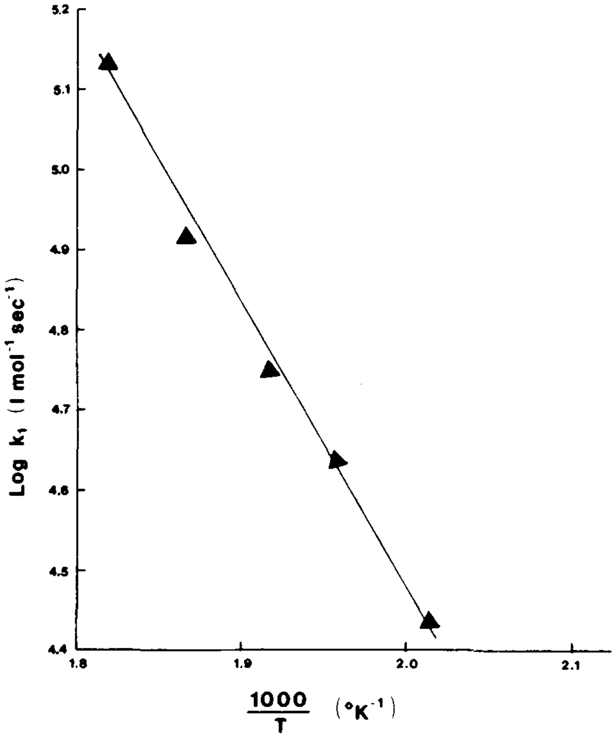

Figure 2. Arrhenius plot for the reaction $CH_3CF_2I + I \rightarrow CH_3\dot{C}F_2 + I_2$.

CH_3CF_2I shown in Table II confirmed that the reaction proceeded with the expected stoichiometry.

An Arrhenius plot of the data for k_1 is shown in Figure 2, and a least squares analysis of the data yields

$$\text{(III)} \qquad \log k_1(M^{-1} \cdot \text{sec}^{-1}) = (11.4 \pm 0.3) - \frac{(15.7 \pm 0.8)}{\theta}$$

In eq. (III) $\theta = 2.303\ RT$ kcal/mole and the errors are standard deviations. The logarithm of the observed A factor agrees well with values reported for similar reactions, namely, 11.4 for CH_3I [3], 10.8 for CF_3I [5], 11.0 for C_2H_5I [11]. 11.5 for CF_3CH_2I [7], and 11.2 for CF_3CF_2I [8]. The observed data for k_2/k_3 are scattered. However, it is well known that $E_3 - E_2 = 1 \pm 1$ kcal/mole [1] so that with this assumption

$$\text{(IV)} \qquad \log \frac{k_2}{k_3} = (0.45 \pm 0.07) + \frac{1}{\theta}$$

Here also, $\log A_2/A_3$ is in good agreement with previously reported values: 0.5 for CH_3I [3], 0.69 for CF_3I [5], 0.6 for C_2H_5I [11], 0.65 for CF_3CH_2I [7], and 0.68 for CF_3CF_2I [8].

From the observed activation energy E_1 and the assumption that $E_2 = 0 \pm 1$ kcal/mole, it follows that

$$\text{(V)} \qquad \Delta H_r^\circ(1{,}523\text{K}) = 15.7 \pm 1.0 \text{ kcal/mole}$$

The heat capacities of CH_3CF_2I [12] and CH_3CF_2 were estimated by group additivity [13] at 500 and 298K so that $\overline{\Delta C_p}^\circ = -0.8 \pm 0.5$ cal/°K · mole. Therefore,

$$\text{(VI)} \qquad \Delta H_r^\circ(1{,}298\text{K}) = 15.9 \pm 1 \text{ kcal/mole}$$

Combining this result with $DH^\circ(\text{I–I}) = 36.2$ kcal/mole [14], one finds that

$$\text{(VII)} \qquad DH^\circ(CH_3CF_2\text{–I}) = 52.1 \pm 1 \text{ kcal/mole}$$

These results are certainly in line with previous studies of the C–I bond energy in alkyl iodides, for example, CH_3CH_2I (53.3 kcal/mole) [11], CF_3CH_2I (56.3 kcal/mole) [7], and CF_3CF_2I (52.5 kcal/mole) [8]. From this, one can conclude that the C(sp^3)–I bond is relatively insensitive to substituent effects. In contrast, however, the C–I bond energy in iodobenzene [15], a C(sp^2)–I bond, was found to be 65 ± 1 kcal/mole. This is a strengthening of about 20% and seems much too large an effect to be simply ascribed to hybridization alone. Thus these data suggest considerable double-bond character in the C–I bond in iodobenzene, and this is qualitatively in accord with the shorter C–I bond distance in iodobenzene [16] as compared to alkyl iodides [17].

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