π Bond Dissociation Energy in 1,1-Difluoroethylene

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Abstract: The π bond dissociation energy of an unsymmetrical olefin such as 1,1-difluoroethylene may be defined by two, not necessarily equivalent, equations; namely, $D\pi°(CF_2{=}CH_2) = DH°(CF_3CH_2\text{-}X) - DH°(\dot{C}F_2CH_2\text{-}X)$ and $D\pi°(CF_2{=}CH_2) = DH°(CH_3CF_2\text{-}X) - DH°(\dot{C}H_2CF_2\text{-}X)$. It has recently been shown that $D\pi°(CF_2{=}CH_2) = 62.1 \pm 1.5$ kcal/mol using the first equation with X = Br. In this work, recent bond dissociation energy data are combined with the necessary thermochemistry to derive an independent value of the π bond dissociation energy of 1,1-difluoroethylene by the second equation with X = F; this yields $D\pi°(CF_2{=}CH_2) = 62.8 \pm 2$ kcal/mol confirming, not only the transferability of the π bond dissociation energy, but also the unusually high value (when compared with tetrafluoroethylene and ethylene) found for this olefin. This high value is further shown to be qualitative consistent with the reactivity of 1,1-difluoroethylene in reactions which break this π bond.

In 1965, Benson[1] defined the π bond dissociation energy in a simple olefin as the difference in the bond dissociation energy of a given bond in the relevant saturated compound and in the β free radical. Thus, the π bond dissociation energy (πBDE) in ethylene was defined as:

$$D\pi°(CH_2{=}CH_2) = DH°(CH_3CH_2\text{-}H) - DH°(\dot{C}H_2CH_2\text{-}H) \quad \text{(i)}$$

which can be generalized to:

$$D\pi°(CH_2{=}CH_2) = DH°(CH_3CH_2\text{-}X) - DH°(\dot{C}H_2CH_2\text{-}X) \quad \text{(ii)}$$

However, in the case of an unsymmetrical π bond such as in 1,1-difluoroethylene (or formaldehyde) there are two possible definitions, namely:

$$D\pi°(CF_2{=}CH_2) = DH°(CF_3CH_2\text{-}X) - DH°(\dot{C}F_2CH_2\text{-}X) \quad \text{(iii)}$$

and

$$D\pi°(CF_2{=}CH_2) = DH°(CH_3CF_2\text{-}X) - DH°(CH_2CF_2\text{-}X) \quad \text{(iv)}$$

While there is no inherent reason for eq iii and iv to yield equivalent results, the utility of the πBDE will be greatly enhanced if this is so.

We have recently determined $D\pi°(CF_2{=}CH_2) = 62.1 \pm 1.5$ kcal/mol[2] from eq iii with X = Br, and it is now possible to combine recent bond dissociation energy data on 1,1,1-trifluoroethane[3] and 1,1-difluoroethane[4] with appropriate thermodynamic data to derive $D\pi°(CF_2{=}CH_2)$ from eq iv with X = F. This provides a test of the equivalence of eq iii and iv as well as possible confirmation of the unexpectedly strong πBDE found for 1,1-difluoroethylene.

Results and Discussion

We have recently determined $\Delta H_f°(CH_3CF_2,g,298) = -72.3 \pm 2$ kcal/mol from which we derived:[4]

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

In addition $\Delta H_f°(CF_3\dot{C}H_2,g,298) = -123.6 \pm 1$ kcal/mol[3] may be combined with $\Delta H_f°(CF_2{=}CH_2,g,298) = -80.5 \pm 1$ kcal/mol[5] and $\Delta H_f°(F,g,298) = 18.9$ kcal/mol[6] to yield $DH°(CH_2CF_2\text{-}F) = \Delta H_f°(CF_2{=}CH_2,g,298) + \Delta H_f°(F,g,298) - \Delta H_f°(CF_3CH_2,g,298) = 62.0 \pm 2$ kcal/mol. Thus, from eq iv with X = F, we have

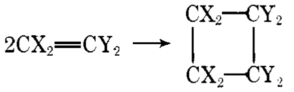
$$D\pi°(CF_2{=}CH_2) = 62.8 \pm 2 \text{ kcal/mol}$$

in excellent agreement with the result $D\pi°(CF_2{=}CH_2) = 62.1 \pm 1.5$ kcal/mol derived from the kinetics of bromination[2] and based on eq iii with X = Br. Thus, independent values of the πBDE in 1,1-difluoroethylene from eq iii and iv are in excellent agreement confirming, not only the transferability of πBDE for unsymmetrical olefins, but also the value thus obtained. The preferred value becomes $D\pi°(CF_2{=}CH_2) = 62.5 \pm 1$ kcal/mol.

Free radical reactivity has frequently been related either to the difference in bond dissociation energies[7] (i.e., the heat of a reaction) or to the bond dissociation energies themselves[8] and olefins are not expected to be exceptions.[9,10] The strong πBDE in $CF_2{=}CH_2$ relative to those for $CH_2{=}CH_2$ (59.0 kcal/mol)[1] and $CF_2{=}CF_2$ (52.5 kcal/mol)[11] would be expected to correlate with a decreased reactivity of $CF_2{=}CH_2$ in reactions breaking the π bond. This is certainly the case in free radical addition reactions for which the reactivity of $CF_2{=}CH_2$ is not only lower than those of $CH_2{=}CH_2$ and $CF_2{=}CF_2$ but also corresponds to a minimum in the total reactivity for the series of olefins $C_2H_{4-n}F_n$ as n goes from 0 to 4.[12]

Another interesting class of reactions is the 2 + 2 cycloadditions for which $CF_2{=}CF_2$ readily forms the perfluorocyclobutane dimer[13] while $CF_2{=}CH_2$ apparently does not.[14]

The thermochemistry of the head-to-head dimerization of an olefin, $CX_2{=}CY_2$ (reaction 1)



$$2CX_2{=}CY_2 \longrightarrow \begin{matrix} CX_2{-}CY_2 \\ | \quad\quad | \\ CX_2{-}CY_2 \end{matrix} \quad (1)$$

is given by

$$\Delta H_r° = 2D\pi°(CX_2{=}CY_2) + E_s - DH°(\text{-}CX_2\text{-}CX_2\text{-}) - DH°(\text{-}CY\text{-}CY_2\text{-}) \quad \text{(v)}$$

in which E_s is the ring strain energy for the four-member ring; for cyclobutanes E_s is 26.2 kcal/mol.[15] This equation may be tested on the dimerization of $CH_2{=}CH_2$ (X = Y = H), for which $\Delta H_r° = -18.2$ kcal/mol,[5] and $CF_2{=}CF_2$ (X = Y = F), for which $\Delta H_r° = -50$ kcal/mol.[16] Thus, $DH°(\text{-}CH_2\text{-}CH_2\text{-}) = 81.5$ kcal/mol[17] and $DH°(\text{-}CF_2\text{-}CF_2\text{-}) = 89.5$ kcal/mol[11] so that eq v yields $\Delta H_r° = -18.8$ kcal/mol for $CH_2{=}CH_2$ dimerization and $\Delta H_r° = -47.8$ kcal/mol for $CF_2{=}CF_2$ dimerization, both in good agreement with the experimental values. Thus, eq v predicts $\Delta H_r° = -19.8$ kcal/mol for the dimerization of $CF_2{=}CH_2$, a value surprisingly close to that for ethylene.

The activation energy for the dimerization of $CF_2{=}CF_2$ is 25 ± 1 kcal/mol[13,18] and that for the dimerization of $CH_2{=}CH_2$ is 44.3 kcal/mol, based on the reverse activation energy[19] and thermochemistry.[5,15] Thus, the activation energy for dimerization increases with πBDE so that for the dimerization of $CF_2{=}CH_2$, the activation energy should be greater than 44 kcal/mol.

The activation energy for the dimerization of $CH_2{=}CH_2$ with $CH_2{=}O$ ($D\pi^\circ = 71$ kcal/mol[1,5,17]) may be calculated from the reverse reaction[19] and thermochemistry.[5,15] This yields 54 kcal/mol, which suggests that the activation energy for the dimerization of $CF_2{=}CH_2$, with $D\pi^\circ = 62.5$ kcal/mol, may be several kcal/mol greater than that for ethylene. Thus, with a reactivity considerably less than that of ethylene but a thermochemistry about the same, it is evident that, at temperatures where the thermal 2 + 2 cycloaddition reaction of $CF_2{=}CH_2$ will be fast, the equilibrium will favor the monomer so that the thermal dimerization (at ordinary pressures) is not expected.

These considerations show that the high values for the πBDE in 1,1-difluoroethylene confirmed in this work are qualitatively consistent with the reactivity of this olefin in addition reactions.

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Interaction of Hydrogen, Carbon, Ethylene, Acetylene, and Alkyl Fragments with Iron Surfaces. Catalytic Hydrogenation, Dehydrogenation, Carbon Bond Breakage, and Hydrogen Mobility

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Abstract: Interactions of hydrocarbons with iron surfaces are analyzed with theoretical calculations. The catalyzed breakings of carbon-carbon, carbon-hydrogen, and H_2 bonds are demonstrated. The interactions of hydrogen and carbon atoms with an iron atom on the surface weaken iron-iron bonds. Calculated geometries for ethylene and acetylene bonded to single iron atoms are similar to those in complexes. On the surface these molecules tend to dissociate into CH_2 and CH fragments. These in turn dehydrogenate with low activation energies calculated to be in the order of 20 kcal/mol. Adsorption energies for the hydrocarbons depend to a considerable extent on the iron 4s and 4p atomic orbitals, which stabilize the lowest lying σ framework hydrocarbon orbital.

I. Introduction

There is need for interplay between theory and experiment in the burgeoning field of surface chemisorption and catalysis. Neither experimental nor theoretical studies have given anything more than a rudimentary characterization of geometric structures and electronic and vibrational properties of surface systems. Even less is known about reaction mechanisms in surface catalysis. From the current experimental end, combinations of LEED, photoemission, work function, and electron induced ion desorption and flash desorption studies can lead to reasonable guesses of overlayer species and structures, on single crystal faces. Some infrared studies of species adsorbed to supported microcrystalline metal catalysts and thin metal films have shown shifts in adsorbate bond stretching frequencies due to interactions with the metal. Infrared techniques are not yet sensitive enough for use with single crystal faces. Despite the lack of unequivocal spectroscopic techniques for use in surface studies at present, data are being gathered, using the above techniques, by many laboratories. These data are pieces of a puzzle of concern to the experimental workers and to those wishing to develop theoretical procedures for understanding and predicting surface phenomena.

In this paper hydrocarbon interactions with iron are studied theoretically. There is only limited information about structures, absorbate energy levels, reaction pathways, and reaction activation energies of hydrocarbons on iron surfaces. In this paper model molecular orbital calculations are presented using one to five iron atoms. The important orbital interactions between adsorbates and these clusters are displayed and discussed. Changes in the positions of the energy levels are depicted as functions of geometric distortions of adsorbate molecules. Energy curves for HH, CC, and CH bond breaking are calculated. The ability of iron to catalytically break and form these bonds is demonstrated and discussed.

The theory[1] has two steps. First, rigid atoms are superimposed and the Hellmann-Feynman force formula is used to