A High-Level Computational Study on the Thermochemistry of Vinyl and Formyl Halides: Heats of Formation, Dissociation Energies, and Stabilization Energies

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The heats of formation, $\Delta H_{f\,298}$, of vinyl and formyl halides calculated using G2 theory are −145.9 (CH_2-CHF), 21.8 (CH_2CHCl), 79.6 (CH_2CHBr), 147.1 (CH_2CHI), −393.7 (HFCO), −192.7 (HClCO), −133.9 (HBrCO), and −66.2 kJ mol^{-1} (HICO), which agree with the available experimental data. While the covalent radii of sp^3 and sp^2 hybridized carbons are 0.762 and 0.735 Å, respectively, at the MP2/6-31G(d) level, the C−X bond lengths in formyl bromide and iodide are 0.016 and 0.045 Å, respectively, *longer* when compared with those in methyl bromide and iodide. However, the C−F bond in formyl fluoride is 0.040 Å shorter than the C−F bond in methyl fluoride. The C−X bond dissociation energies (D_{C-X}) for vinyl, formyl, and methyl halides show good linear correlations with the Mulliken and Pauling electronegativites of the halogens. The D_{C-X} values for formyl bromide and iodide are *smaller* than those calculated for methyl bromide and iodide. The stabilization energies (SE) yielding estimates of the stabilization of the C═C and C═O double bonds by halogens decrease from X = F to X = I and show reasonable linear correlations with the Mulliken and Pauling electronegativities of the halogens. While the D_{C-X} energies for formyl halides are smaller than those for vinyl halides, the SE(formyl) values are larger than the corresponding SE(vinyl). The elimination of HX from formyl halides is exothermic, in contrast to the endothermic elimination of HX from vinyl halides.

1. Introduction

The thermochemistry of vinyl and formyl halides is of particular importance because these are prototypical molecules containing vinylic and carbonyl carbons, respectively, and exemplify features of these classes of organic compounds. Stabilization energies calculated from the enthalpies of isodesmic[2] reactions 1 and 2 provide estimates of the C═C and C═O double bond stabilizations by halogens.[3−6] One of the reasons why these stabilization energies attract the interest of chemists is that it provides an opportunity to evaluate the "element effect."[4,7−11] The "element effect", first introduced by Bunnett for the study of nucleophilic aromatic substitution,[12] is a useful tool[4,7−11] that can potentially be used to distinguish between stepwise and concerted processes in nucleophilic substitutions at vinylic and carbonyl carbons. Both these reactions are characterized by a wide spectrum of reaction mechanisms.[7,8,13−17]

$$H_2C{=}CHX + CH_4 \rightarrow H_2C{=}CH_2 + CH_3X \qquad (1)$$

$$O{=}CHX + CH_4 \rightarrow O{=}CH_2 + CH_3X \qquad (2)$$

The C−X bond dissociation energies (X = F to I) of vinyl and formyl halides (eqs 3 and 4) are of considerable interest since these collective data for the entire group of the halogens reflect the effect of the ionic character of the bond on its dissociation energy.[18] Formyl halides can be formed by the tropospheric degradation of chlorofluorocarbon (CFC) species[19] such as CF_3CHXY (X, Y = H, F, Cl), and the energetics of their degradations via, for example, reactions 4 and 5 has been the subject of many studies.[20,21] Gas-phase decompositions of vinyl halides (eq 6) yield data on the reverse bimolecular addition of HX to acetylene,[22] which is a key example of an electrophilic addition reaction in organic chemistry.

$$H_2C{=}CHX \rightarrow H_2C{=}CH^\bullet + X^\bullet \qquad (3)$$

$$O{=}CHX \rightarrow OCH^\bullet + X^\bullet \qquad (4)$$

$$O{=}CHX \rightarrow OC + HX \qquad (5)$$

$$H_2C{=}CHX \rightarrow HC{\equiv}CH + HX \qquad (6)$$

However, both the experimental and computational thermochemical data on vinyl and formyl halides are incomplete and, in some cases, controversial. The experimental heats of formation are known only for vinyl fluoride, chloride, and bromide, as well as for HFCO. Very few experimental enthalpies of reactions 1−6 are available. Furthermore, computational estimates of the stabilization energies (eqs 1 and 2) are inconsistent. For example, the stabilization energies calculated at the HF/4-31G(d) level using the bond-separation isodesmic reaction 1 indicate that the stabilizing effect of chlorine is about twice that of fluorine.[3a] These data are in disagreement with experimental estimates that show the opposite order.[4,8]

In the present paper, we have considered the thermochemistry of vinyl and formyl halides for the entire set of halogens from F to I and at a much higher computational level than that used in the earlier calculations. We have used G2 theory[23] that has been recently extended for bromine- and iodine-containing molecules using effective core potentials (ECP).[24] This modification of G2 theory is denoted as G2(ECP).[24,25]

2. Computational Methods

Ab initio molecular orbital calculations[2] were carried out using G2 theory[23] with the GAUSSIAN-94 system of programs.[26] G2 theory corresponds effectively to calculations at the QCISD(T)/6-311+G(3df,2p) level with zero-point vibrational energy (ZPE) and higher level corrections.[23] For bromine- and iodine-containing species, the extended G2 scheme,[24] based

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TABLE 1: Calculated G2 Total Energies (hartrees) for Species Involved in Reactions 1−6[a]

	E_{tot}			E_{tot}	
species	0 K	298 K	species	0 K	298 K
$H_2C{=}CHF$	−177.572 08	−177.567 77	HF	−100.350 01[b]	
$H_2C{=}CHCl$	−537.568 28	−537.563 78	HCl	−460.340 17[b]	
$H_2C{=}CHBr$	−91.174 92	−91.170 27	HBr	−13.945 10	
$H_2C{=}CHI$	−89.190 52	−89.185 76	HI	−11.961 64	
$H_2C{=}CH_2$	−78.415 93[b]		H_3CF	−139.554 21[b]	
$H_2C{=}CH^{\bullet}$	−77.739 96[b]		H_3CCl	−499.553 83[b]	
$HC{\equiv}CH$	−77.185 74[b]		H_3CBr	−53.162 83	
$O{=}CHF$	−213.524 35	−213.520 38	H_3CI	−51.182 84	
$O{=}CHCl$	−573.507 89	−573.503 70	H_4C	−40.410 88[b]	
$O{=}CHBr$	−127.114 17	−127.109 83	$H_3C^{\bullet}$	−39.745 09[b]	
$O{=}CHI$	−125.129 70	−125.125 23	$F^{\bullet}$	−99.632 82[b]	
$O{=}CH_2$	−114.338 88[b]		$Cl^{\bullet}$	−459.676 64[b]	
$O{=}CH^{\bullet}$	−113.698 83[b]		$Br^{\bullet}$	−13.308 71	
OC	−113.177 49[b]		$I^{\bullet}$	−11.351 84	

[a] G2(ECP) energies are given for Br- and I-contaning species. [b] Taken from ref 23.

on the quasi-relativistic effective core potentials (ECP) developed by the Stuttgart group,[27] was used (G2(ECP)).[25] Geometries were optimized at the HF and MP2 levels using analytic gradient techniques.[28] The stationary points on the potential energy surfaces were characterized by calculations of vibrational frequencies, which were done analytically for X = F, Cl and numerically in ECP calculations of bromine- and iodine-containing species. The heats of formation were calculated[29] from the atomization energies using the experimental heats of formation of atoms.[30] To obtain theoretical heats of formation at 298 K, vibrational contributions to temperature corrections[2] were calculated with the use of harmonic frequencies computed at the HF/6-31G(d) level and scaled by 0.8929 according to the G2 scheme.[23] Experimental temperature corrections for atoms, taken from ref 31, were used.

Unless stated otherwise, we have used the results of G2 calculations for F- and Cl-containing molecules and G2(ECP) calculations for Br- and I-containing molecules in our analysis. Throughout this paper, relative energies are presented as enthalpy changes (ΔH) at 0 K, bond lengths are in angstroms, and bond angles are in degrees. G2 total energies of vinyl and formyl halides as well as of the species involved in reactions 1−6 are listed in Table 1.

3. Results and Discussion

Geometries. The geometries of the vinyl and formyl halides calculated at the MP2/6-31G(d) as well as the available experimental data are given in Tables 2 and 3. A comparison of the geometries of vinyl fluoride, chloride, and bromide calculated at various computational levels with the experimental structural data was reported earlier.[33,35] The calculated geometries of formyl fluoride and chloride (Table 3) are in reasonable agreement with experimental geometrical parameters, although elongations of the C−F and C−Cl bond lengths by 0.006 and 0.017 Å, respectively, as compared with the experimental values,[39,40] are notable. The C═C and C═O bonds in vinyl and formyl halides are shortened slightly when compared with those in ethylene and formaldehyde, respectively (Tables 2 and 3). The C═C bond lengths in vinyl halides increase from 1.330 Å (X = F) to 1.334 Å (X = I), and the CCX bond angles show a small widening from 121.4° (X = F) to 123.1° (X = I) (Table 2). However, there are no systematic changes in the C═O bond lengths in formyl halides, induced by a variation of the substituent from X = F to X = I (Table 3). The widening of the OCX bond angle in formyl halides is quite insignificant, from 123.2° for X = F to 123.8° for X = I. The variations in the C−H bond lengths from X = F to X = I in both vinyl and formyl halides are quite small (Tables 2 and 3).

The covalent radii of sp^3 and sp^2 hybridized carbons are 0.762 and 0.735 Å, respectively, at the MP2/6-31G(d) level.[18] These values are close to the experimental estimates of 0.766 and 0.738 Å.[18] Therefore, it should be expected that the C−X bond lengths in vinyl and formyl halides are shorter than those in methyl halides. Indeed, these bond lengths in the vinyl halides are shortened as compared with those in methyl halides (Table 4). It is notable that for X = F the difference in the C−X bond lengths in vinyl and methyl halides is 0.026 Å, which is almost the difference in the covalent radii for sp^3 and sp^2 hybridized carbons (0.027 Å). However, the C−X bond differences for X = Cl to I are almost twice as large (0.048 Å (Cl), 0.049 Å (Br), and 0.046 Å (I); Tables 2 and 4). The C−X bond length differences between formyl and methyl halides display a more pronounced variation. The most remarkable finding is that C−X bond lengths in formyl bromide and iodide are 0.016 and 0.045 Å, respectively, *longer* when compared with those in methyl bromide and iodide (Tables 3 and 4), in contrast to the aforementioned values of the covalent radii of sp^3 and sp^2 hybridized carbons. In contrast to the C−Br and C−I bond lengths, the C−F bond in formyl fluoride is 0.040 Å shorter than the C−F bond in methyl fluoride (Figure 1). It is also notable that the difference between the C−X bond lengths in formyl and methyl halides changes by almost equal increments of 0.028 Å and demonstrates a reasonably linear correlation with the Mulliken electronegativities[40] of the halogens ($r^2 = 0.925$). As shown below, the elongations of the C−X bonds in formyl bromide and iodide, as compared with the lengths of these bonds in $H_3C{-}Br$ and $H_3C{-}I$, look reasonable in light of the smaller C−X bond dissociation energies (D_{C-X}) for formyl bromide and iodide than the D_{C-X} values for methyl bromide and iodide.

Heats of Formation. The G2 calculated heats of formation for vinyl and formyl halides are given in Table 5. The G2 $\Delta H_{f\,298}$ values agree with the experimental values which are available only for CH_2CHX (X = F to Br) and for formyl fluoride. The indirect estimate[30] of a $\Delta H_{f\,298}(CH_2CHI)$ of 130 kJ mol^{-1} seems to be too low when compared with the G2 value of 147.1 kJ mol^{-1}. The $\Delta H_{f\,0}$ values for formyl fluoride and chloride calculated using G2 theory (−390 and −189.5 kJ mol^{-1}, respectively) are close to the values of −392.5 ± 6.3 and −190.4 ± 6.3 kJ mol^{-1} calculated from the energies of isodesmic reactions at the MP4/6-311++G(2df,2p)//MP2/6-311G(2d,2p) level.[47] The heat of formation for CH_2CHCl, calculated using G2 theory ($\Delta H_{f\,298} = 21.8$ kJ mol^{-1}), agrees very well with the experimental $\Delta H_{f\,298}$ (CH_2CHCl) value[30] of 23 ± 2 kJ mol^{-1}. Our G2 calculations corroborate the conclusion based on the G2 calculations of the energy of the bond-separation reaction for vinyl chloride[6a] that the experimental value of $\Delta H_{f\,298}(CH_2CHCl)$ given in ref 48 as 37.3 ± 1.3 kJ mol^{-1} is incorrect.

Bond Dissociation Energies. As seen from Table 6, the C−X bond dissociation energies (D_{C-X}) for vinyl halides are larger than those for the formyl and methyl halides.[49] The C−X bond energies for the methyl halides serve as the reference BDEs because these bonds are considered to be appropriate models for normal C−X bonds.[6a] The increase in the C−X bond strength from X = I to X = F (Figure 2) can be attributed to the increasing ionic character of the bonds, which results in a Coulombic stabilization.[5,6,18] Indeed, the D_{C-X} values for vinyl, formyl, and methyl halides show good linear correlations with the Mulliken and Pauling electronegativites of halogens (Table 7). The strength of the formyl C−X bonds vary in a range of 298.4 kJ mol^{-1}, which is 34.3 and 61.1 kJ mol^{-1} wider than

TABLE 2: Calculated and Experimental Geometries of Vinyl Halides, CH_2CHX (X = F to I) as Well as for Ethylene (X = H)

molecule	computational level	R(C=C)	$R(C_a-X)$	$R(C_a-Ha)$	$R(C_b-Hb)$	$R(C_b-Hc)$	$\angle C_bC_aX$	$\angle C_bC_aH_a$	$\angle C_aC_bH_b$	$\angle C_aC_bH_c$
ethylene	MP2/6-31G(d)	1.335	1.085	1.085	1.085	1.085	121.7	121.7	121.7	121.7
ethylene	exptl[a]	1.339	1.085	1.085	1.085	1.085	121.8	121.8	121.8	121.8
X = F	MP2/6-31G(d)	1.330	1.366	1.084	1.083	1.083	121.4	127.1	121.6	119.1
X = F	exptl[b]	1.329	1.346	1.077	1.081	1.081	121.5	125.4	120.9	118.6
X = Cl	MP2/6-31G(d)	1.332	1.730	1.083	1.084	1.083	123.2	123.6	122.2	119.5
X = Cl	exptl[c]	1.331	1.732	1.078	1.084	1.082	122.6	123.6	121.1	118.9
X = Br	MP2/6-31G(d)-ECP	1.332	1.901	1.084	1.083	1.085	122.7	124.5	122.6	119.3
X = Br	MP2/6-31G(d)-AE[d]	1.331	1.897	1.085	1.083	1.085	122.9	124.3	122.5	119.5
X = Br	exptl[c]	1.330	1.890	1.077	1.085	1.083	122.5	124.2	121.3	118.7
X = I	MP2/6-31G(d)-ECP	1.334	2.115	1.084	1.084	1.087	123.1	123.8	123.0	119.3

[a] Taken from ref 32. [b] Experimental r_0 structure obtained by weighted fit[33] to data of microwave study of vinyl fluoride.[34] [c] Experimental r_0 structure obtained by weighted fit[35] to data of microwave study of vinyl chloride[36] and vinyl bromide.[37] [d] Taken from ref 35.

TABLE 3: Calculated and Experimental Geometries of Formyl Halides as Well as of Formaldehyde

molecule	computational level	R(C=O)	R(C−X)	R(C−H)	∠OCX	∠HCX
$H_2C{=}O$	MP2/6-31G(d)	1.220	1.104	1.104	122.2	115.6
	exptl[a]	1.203 ± 0.003	1.099 ± 0.009	1.099 ± 0.009	121.8 ± 1.2	116.5 ± 1.2
X = F	MP2/6-31G(d)	1.194	1.352	1.094	123.2	109.2
X = F	exptl[b]	1.188 ± 0.004	1.346 ± 0.003	1.11 ± 0.02	122.3 ± 0.2	107 ± 4
X = Cl	MP2/6-31G(d)	1.199	1.767	1.096	123.7	110.0
X = Cl	exptl[c]	1.182	1.765	1.090	123.1	110.4
X = Br	MP2/6-31G(d)-ECP	1.195	1.966	1.096	123.7	109.0
X = I	MP2/6-31G(d)-ECP	1.195	2.206	1.097	123.8	109.2

[a] Experimental r_e structure was taken from ref 38. [b] Experimental r_g bond lengths and r_{av} angles.[39] [c] r_e structure was taken from ref 40.

TABLE 4: Calculated and Experimental Geometries of Methyl Halides

molecule	computational level	R(C−X)	R(C−H)	∠HCX
H_3CF	MP2/6-31G(d)	1.392	1.092	109.1
H_3CF	exptl[a]	1.383	1.086	108.8
H_3CCl	MP2/6-31G(d)	1.779	1.088	108.9
H_3CCl	exptl[b]	1.776	1.085	108.6
H_3CBr	MP2/6-31G(d)-ECP	1.950	1.087	107.9
H_3CBr	exptl[c]	1.934	1.082	107.7
H_3CI	MP2/6-31G(d)-ECP	2.161	1.087	107.8
H_3CI	exptl[d]	2.132	1.085	108.6

[a] From ref 42. [b] From ref 43. [c] From ref 44. [d] From ref 45.

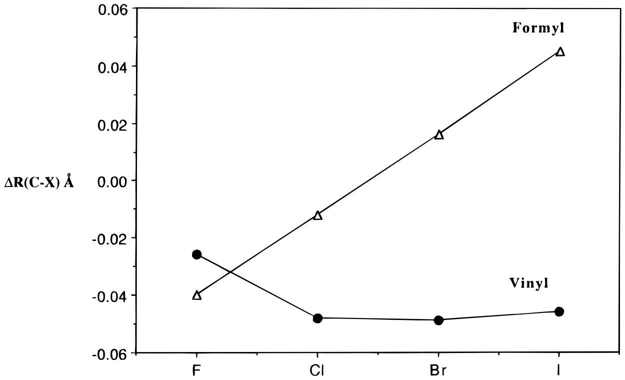

Figure 1. Differences between the C−X bond lengths (in angstroms) in vinyl halides and methyl halides (●) as well as between the C−X bond lengths in formyl halides and methyl halides (△), calculated at the MP2/6-31G(d) level. The C−X bond lengths are given in Tables 2−4.

TABLE 5: G2 Heats of Formation of Vinyl and Formyl Halides (in kJ mol^{-1}) as Well as Experimental Values[a]

molecule	G2 $\Delta H_{f\,0}$	G2 $\Delta H_{f\,298}$	exptl $\Delta H_{f\,298}$
vinyl fluoride	−137.9	−145.9	−138.8 ± 1.7
vinyl chloride	29.3[b]	21.8	23 ± 2
vinyl bromide	94.4[c]	79.6	79.3 ± 1.9
vinyl iodide	156.0	147.1	130[d]
formyl fluoride	−390.0	−393.7	−377
formyl chloride	−189.5	−192.7	
formyl bromide	−123.5	−133.9	
formyl iodide	−61.7	−66.2	

[a] Taken from ref 30. [b] Experimental value[30] of $\Delta H_{f\,0}$ is 31 kJ mol^{-1}. [c] Experimental value[30] of $\Delta H_{f\,0}$ is 94.2 kJ mol^{-1}. [d] Estimated value.[31] Other estimates[51] are 142.7 ± 5.9 and 136.0 kJ mol^{-1}.

TABLE 6: C−X Bond Dissociation Enthalpies in Vinyl, Formyl, and Methyl Halides Calculated Using G2 Theory[a]

X	vinylic D_{C-X}	formylic D_{C-X}	methyl D_{C-X}
F	523.3 (520.0)[b]	505.9	462.9 (465.4)[e]
Cl	398.2 (400.4)[b]	347.7	346.8 (342.0)[e]
Br	331.5[c] (342.4)[b]	280.0	286.3 (289.9)[e]
I	259.2 (281.0)[b,d]	207.5	225.6 (231.2)[e]

[a] In kJ mol^{-1}. [b] Experimental D_{C-X} values for vinyl halides calculated using the $\Delta H_{f\,0}$ data taken from ref 30 are given in parentheses. The experimental $\Delta H_{f\,0}$ value of vinyl radical was taken from ref 50b. [c] Another experimental estimate of the D_{C-Br} value[46] is 322.2 ± 12.6 kJ mol^{-1}. [d] The experimental $\Delta H_{f\,0}(C_2H_3I)$ value given in ref 30 differs from other experimental estimates and the G2 calculated $\Delta H_{f\,0}$ value; see Table 5. [e] Experimental D_{C-X} values for methyl halides calculated using the $\Delta H_{f\,0}$ data taken from ref 30 are given in parentheses.

the ranges of the variations for the D_{C-X} values in vinyl and methyl halides, respectively (Table 6). Therefore, the electronegativity effects on the D_{C-X} values are enhanced in formyl halides as compared with vinyl and methyl halides. Indeed, the differences in the D_{C-X} values for formyl and methyl halides as well as for vinyl and methyl halides decrease from X = F to X = I and show linear correlations with the Mulliken electronegativites of the halogens (Table 7). The stronger C−X bonds in vinyl halides when compared with those in H_3CX could be considered as a consequence of the difference in the hybridizations of the vinylic and methyl carbons.[6] If this is the case, a similar relationship for the C−X bond strength should be expected for formyl and methyl halides. However, the C−Br and C−I bonds in formyl halides are 6.3 and 18.1 kJ mol^{-1} *weaker* than those of the methyl halides (Figure 3). This trend may be a consequence of the resonance stabilization of the formyl radical. The difference between the D_{C-X} values for formyl and methyl halides does correlate with the difference in the C−X bond lengths for these molecules (Table 7).

Stabilization Energies. The energies of the isodesmic bond-separation reactions 1 and 2 yield estimates of stabilization of

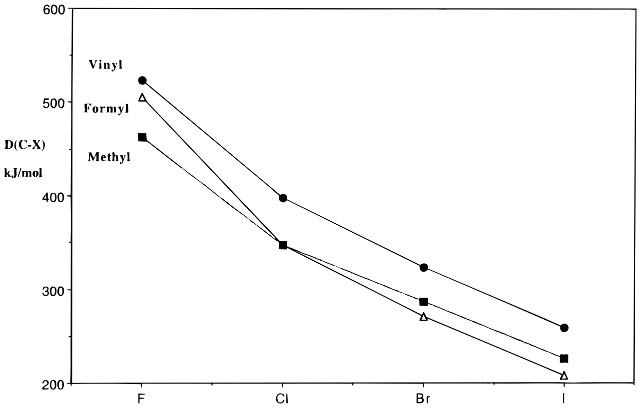

Figure 2. C−X bond strength in vinyl (●), formyl halides (△), and methyl halides (■) calculated using G2 theory. The D_{C-X} values are given in Table 6.

TABLE 7: Linear Correlations of Various Characteristics of Vinyl and Formyl Halides Calculated Using G2 Theory

entry	parameter 1	parameter 2	r^2
1	ΔR_{C-X}(vinyl−methyl)[a]	Mulliken electronegativity of X[b]	0.925
2	D_{C-X}(vinyl)[c]	Mulliken electronegativity of X	0.986
3	D_{C-X}(vinyl)	Pauling electronegativity of X	0.974
4	D_{C-X}(formyl)	Mulliken electronegativity of X	0.997
5	D_{C-X}(formyl)	Pauling electronegativity of X	0.990
6	D_{C-X}(methyl)	Mulliken electronegativity of X	0.990
7	D_{C-X}(methyl)	Pauling electronegativity of X	0.979
8	D_{C-X}(vinyl)	D_{C-X}(methyl)	0.999
9	D_{C-X}(formyl)	D_{C-X}(methyl)	0.998
10	ΔD_{C-X}(vinyl−methyl)	Mulliken electronegativity of X	0.908
11	ΔD_{C-X}(formyl−methyl)	Mulliken electronegativity of X	0.986
12	SE(vinyl)[d]	Mulliken electronegativity of X	0.910
13	SE(vinyl)	Pauling electronegativity of X	0.888
14	SE(formyl)	Mulliken electronegativity of X	0.985
15	SE(formyl)	Pauling electronegativity of X	0.994
16	SE(vinyl)	D_{C-X}(vinyl)	0.960
17	SE(formyl)	D_{C-X}(formyl)	0.969

[a] The R(C−X) values are listed in Tables 2−4. [b] The Mulliken and Pauling electronegativities of the halogens were taken from ref 41. [c] The D(CX) values are given in Table 6. [d] Stabilization energies are shown in Table 8.

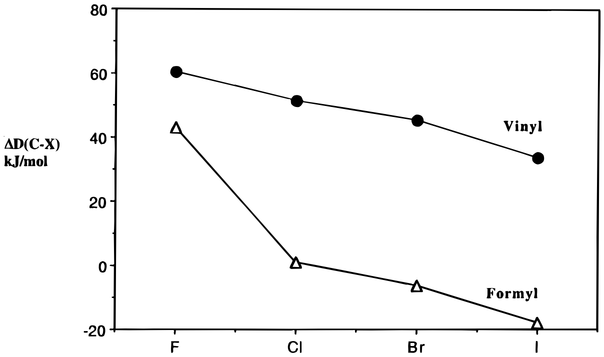

Figure 3. Differences between the C−X bond dissociation energies in vinyl halides and methyl halides (●) as well as between the C−X bond dissociation energies in formyl halides and methyl halides (△), calculated using G2 theory. The D_{C-X} values are shown in Table 6.

TABLE 8: Stabilization Energies of Vinyl Halides and Formyl Halides Calculated Using G2 Theory[a]

X	vinylic SE[b]	formylic SE[c]
F	33.7	110.6
Cl	24.7	68.4
Br	18.5	61.3
I	6.9	49.5

[a] In kJ mol^{-1}. [b] Enthalpy of reaction 1. [c] Enthalpy of reaction 2.

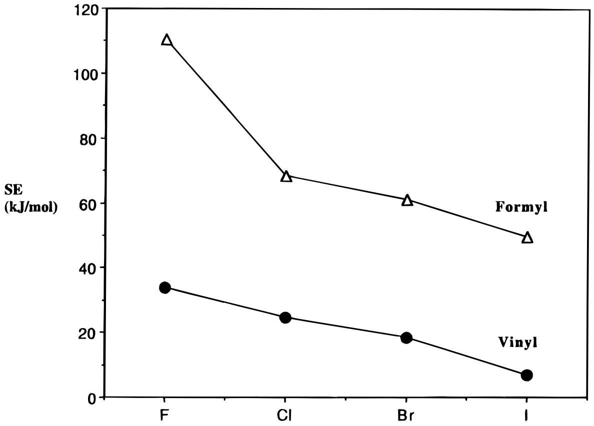

Figure 4. G2 stabilization energies (SE) of vinyl and formyl halides. The SE values are listed in Table 8.

the C=C and C=O double bonds by halogens. These stabilization energies (SE) decrease from X = F to X = I (Table 8) and show reasonable linear correlations with the Mulliken and Pauling electronegativities of halogens (Table 7). The SE(CH_2-CHCl) is 6.2 kJ mol^{-1} larger than the SE for vinyl bromide. This difference in the SE values is close to its experimental estimate[11] of 6.3 kJ mol^{-1} and to the value of 5.4 kJ mol^{-1} found by earlier calculations.[4] It is notable that while the D_{C-X} energies for formyl halides are smaller than the values for vinyl halides (Table 6), the SE(formyl) values are larger than those for SE(vinyl) (Figure 4). The difference in the stabilization energies is maximal for X = F (76.9 kJ mol^{-1}) whereas it is almost the same (about 42−44 kJ mol^{-1}) for the other halogens (Table 8). There is a linear correlation between the vinyl and formyl stabilization energies (Table 7), which, in turn, correlates with the corresponding D_{C-X} values (Table 7).

The stabilization energies provide an estimate of the element effect of the leaving group in nucleophilic substitution at unsaturated carbon.[4] For example, the k_{Br}/k_{Cl} element effect implies that if the rate of the reaction is determined by the addition of the nucleophile in a stepwise process, then the k_{Br}/k_{Cl} ratio should be close to unity. This would suggest that the reaction involves the formation of an intermediate. In contrast, if the k_{Br}/k_{Cl} ratio is considerably larger than unity, it can be a manifestation of either a stepwise mechanism in which either the elimination of the leaving group is rate-determining in the stepwise process or a single-step process is involved. In this case, the element effect should follow the order of the C−X bond strengths (X = F to I).[6] While in most cases experimental estimates of the k_{Br}/k_{Cl} element effect are close to unity,[4,6] our SE values suggest that the k_{Br}/k_{Cl} ratio that should be higher than unity. Therefore, as suggested by Rappoport and co-workers,[4] compensating factors reducing the relative reactivity of the vinyl bromide could operate. As shown by the calculated SE values for the other halogens, this conclusion could be extended to the k_{Cl}/k_F and k_I/k_{Br} element effects.

Energies of HX Elimination from Vinyl and Formyl Halides. The elimination of HX from formyl halides (eq 5) is exothermic, in contrast to the endothermic HX elimination from vinyl halides (eq 6) (Table 9). The enthalpies of reactions 5 and 6 for X = Cl to I do not manifest any clear-cut dependence upon the X = F to I series. The enthalpies for X = Cl to I are very close to each other for reactions 5 and 6.

4. Conclusions

1. The G2 calculated heats of formation, $\Delta H_{f\,298}$, for vinyl and formyl halides are −145.9 (CH_2CHF), 21.8 (CH_2CHCl), 79.6 (CH_2CHBr), 147.1 (CH_2CHI), −393.7 (HFCO), −192.7

TABLE 9: HX Elimination Energies (in kJ mol^{-1}) for Formyl and Vinyl Halides Calculated Using G2 Theory[a]

X	$\Delta H(5)$	$\Delta H(6)$
F	−8.3[b]	95.4
Cl	−25.7	111.2
Br	−22.1	115.7
I	−24.8	113.3

[a] Equations 5 and 6. [b] −10.0 kJ mol^{-1} at the CCSD(T)/DZ+P level.[20a]

(HClCO), −133.9 (HBrCO), and −66.2 kJ mol^{-1} (HICO), which agree with the available experimental values.

2. While the covalent radii of sp^3 and sp^2 hybridized carbons are 0.762 and 0.735 Å, respectively, at the MP2/6-31G(d) level, the C−X bond lengths in formyl bromide and iodide are 0.016 and 0.045 Å, respectively, *longer* when compared with those in methyl bromide and iodide. However, the C−F bond in formyl fluoride is 0.040 Å shorter than the C−F bond in methyl fluoride. The difference between the C−X bond lengths in formyl and methyl halides changes by almost equal increments of 0.028 Å and demonstrates a reasonably linear correlation with the Mulliken electronegativities of the halogens.

3. The $D_{\mathrm{C-X}}$ values for vinyl, formyl, and methyl halides show good linear correlations with the Mulliken and Pauling electronegativities of the halogens. The C−X bond dissociation energies for formyl bromide and iodide are *smaller* than the $D_{\mathrm{C-X}}$ values for methyl bromide and iodide. The C−Br and C−I bond lengths in formyl halides are *longer* as compared with these bond lengths in methyl halides. The difference between the $D_{\mathrm{C-X}}$ values for formyl and methyl halides correlates with the difference in the C−X bond lengths in these molecules.

4. The stabilization energies (SE) of vinyl and formyl halides, which yield estimates of the stabilization of the C═C and C═O double bonds by halogens, decrease from X = F to X = I and show reasonable linear correlations with the Mulliken and Pauling electronegativities of the halogens. While the $D_{\mathrm{C-X}}$ energies for formyl halides are smaller than the values for vinyl halides, the SE(formyl) values are larger than the SE(vinyl).

5. The HX elimination from formyl halides is exothermic, in contrast to the endothermic elimination of HX from vinyl halides.

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