J. Org. Chem. **2001,** *66,* 9041−9042 **9041**

Ab Initio Thermochemistry of Some Halofurans and Halothiophenes

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Received August 7, 2001

Introduction

The purpose of this work is 3-fold. First, we aim to provide accurate $\Delta H_f°$ values for a series of halogenated heteroaromatics for which no data are currently available in the comprehensive literature sources.[1] The chlorinated furans and thiophenes can appear as byproducts in various industrial processes, e.g., metallurgy, manufacture of paper,[2] or in the fly ash from incinerator plant[3] (due to the burning of PVC). The chlorinated furans are carcinogenic, but their carcinogenicity has been studied only recently.[2] It is obviously of interest to study various reactions in which these compounds may be involved in, and so the thermochemical data may be useful. Second, we wish to study relative isomer stability as a function of the type and topology of substitution. Third, we wish to establish whether the thermochemical effects induced by simple halogen substituents can be considered as additive. This work forms part of the series of studies[4−6] which use high-level ab initio calculations together with isodesmic reaction schemes in order to determine accurate $\Delta H_f°$ values and probe thermodynamic stabilities of compounds and the factors which influence them.

Method of Calculation

The ab initio calculations were performed with Gaussian 98 software[7] using G3 method[8] whose typical precision in $\Delta H_f°$(298 K) is ±8.2 kJ/mol. G3 provides total electron energies[9] from which accurate standard enthalpies can be deduced for a wide range of organic compounds using isodesmic or atomization approaches. The selection of "anchor" compounds in isodesmic reactions was made so that only those with accurate and reliable enthalpies were included. The experimental $\Delta H_f°$(298 K) values for "anchor compounds" are C_2H_4 (52.467 kJ mol^{-1}), C_2F_4 (−670.0 kJ mol^{-1}), C_2Cl_4 (−12.426 kJ mol^{-1}), furan (−34.7 kJ mol^{-1}), and thiophene (115.0 kJ mol^{-1}).[1,4−6] These are the most reliable and accurate values at present.

For comparison, the corresponding $\Delta H_f°$(298 K) values obtained by G3 method via atomization approach are C_2H_4 (51.46 kJ mol^{-1}), C_2F_4 (−679.0 kJ mol^{-1}), C_2Cl_4 (−26.8 kJ mol^{-1}), furan (−32.6 kJ mol^{-1}), and thiophene (115.9 kJ mol^{-1}).[1,4−6] One can, of course, select, for example, C_2H_3X ($X = F$, Cl) type compounds as "anchors", but our preference for C_2X_4 stems from the fact that the consistent experimental enthalpies for C_2X_4 "anchors" had been reviewed and checked, unlike C_2H_3X where large discrepancies between measured values exist.[1] The choice of isodesmic, rather than the atomization method for calculating enthalpies, stems from the observation that the isodesmic reaction schemes provide more accurate enthalpies than the atomization approach.[10] This is due to the cancelation of errors in isodesmic reactions. Natural population analysis (NPA) had been performed at MP2(full)/6-31G* level.

Results and Discussion

The following isodesmic reaction schemes (at 298 K) were used for extracting enthalpies:

$$C_2X_4 + 4C_4H_4Y = 4C_4H_3XY + C_2H_4 \quad \text{(for monohalo derivatives)}$$

$$C_2X_4 + 2C_4H_4Y = 2C_4H_2X_2Y + C_2H_4 \quad \text{(for dihalo derivatives)}$$

$$3C_2X_4 + 4C_4H_4Y = 4C_4HX_3Y + 3C_2H_4 \quad \text{(for trihalo derivatives)}$$

$$C_2X_4 + C_4H_4Y = C_4X_4Y + C_2H_4 \quad \text{(for tetrahalo derivatives)}$$

where ($X = F$, Cl; $Y = O$, S).

The procedure for obtaining $\Delta H_f°$(298 K) was as follows. In each isodesmic reaction there are "anchor compounds", with known ΔH_f(298 K) and a single compound whose ΔH_f(298 K) is to be calculated. Enthalpy change in each reaction is given as $\Delta H_r(298\ \text{K}) = \Sigma E_{\text{prod}} - \Sigma E_{\text{react}}$ where E refers to the total energies (including vibrational, and rotational energy contributions at 298 K) obtained from G3 calculations. Subsequently, the unknown ΔH_f(298 K) is calculated from known ΔH_r and ΔH_f(298 K) for "anchor compounds". The absolute enthalpies thus obtained are presented in Table 1 while the decrease in $\Delta H_f°$(298 K) of halogenated heterocycles with respect to their parent heteroaromatic (i.e., furan or thiophene) is shown in Table 2.

The topology of substitution exhibits an interesting influence on relative stabilities of different isomers. Among halofurans, the most stable monohalo, dihalo, and trihalo isomers are 2-, 2,5-, and 2,3,5-, respectively. In halothiophenes, this order is reversed, i.e., the aforementioned isomers become the least stable (Tables 1 and 2). Why does the change of heteroatom reverse isomer stability? Results of NPA analysis show that the partial charges on heteroatoms are of similar magnitude, but opposite signs. Atomic valence populations are of similar

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10.1021/jo0108010 CCC: $20.00

Table 1. Standard Enthalpies of Formation $\Delta H_f°$ (g, 298.15 K)/kJ mol^{-1} for the Compounds $C_4H_{4-x}X_xY$ Where X = F, Cl; Y = O, S

substition	fluoro-furans	chloro-furans	fluoro-thiophenes	chloro-thiophenes
2-	−218.2	−52.6	−49.5	101.5
3-	−203.4	−50.1	−65.6	92.4
2,3-	−373.3	−66.5	−215.1	81.0
2,5-	−394.8	−67.9	−211.3	89.1
2,4-	−387.2	−66.7	−229.2	80.5
3,4-	−360.1	−62.6	−234.1	73.6
2,3,5-	−549.0	−81.0	−374.3	70.0
2,3,4-	−530.4	−78.9	−382.8	62.5
2,3,4,5-	−691.6	−92.8	−525.5	52.7

Table 2. Decrease in $\Delta H_f°$(298 K) for Title Compounds (kJ/mol) vs Parent Furan or Thiophene

substitution	fluoro-furan	chloro-furan	fluoro-thiophene	chloro-thiophene
2-	183.5	17.9	164.5	13.5
3-	168.7	15.4	180.6	22.6
2,3-	338.6	31.8	330.1	34.0
2,4-	352.5	32.0	344.2	34.5
2,5-	360.1	33.2	326.3	25.9
3,4-	325.4	27.9	349.1	41.4
2,3,4-	495.7	44.2	497.8	52.5
2,3,5-	514.3	46.3	489.3	45.0
2,3,4,5-	656.9	58.1	640.5	62.3

magnitude. The charges and valence populations in halofuran isomers fall within the range between −0.52 and −0.57 and 6.50−6.53, respectively. In halothiophene isomers the atomic charges and valence populations are within 0.41−0.53 and 5.41−5.43, respectively. This reversal of charges in halofuran/halothiophene may rationalize the inversion in thermochemical stability of isomers. The reversal of atomic charges can be expected when one considers strongly electronegative oxygen which always carries a negative charge and a much more weakly electronegative sulfur atom. Sulfur and carbon have comparable electronegativity. However, an sp^2 carbon atom bound to halogen is electron deficient and becomes more electronegative. The sulfur atom linked to two such carbons will carry a positive partial charge. The electrostatic interaction between a negative oxygen and two neighboring positive carbons (in halofurans) will be stabilizing, while interaction between positive sulfur and weakly positive carbon neighbors will be destabilizing (in halothiophenes).

The enthalpy decreases with the increasing degree of halogenation. The same trend had been observed in halomethanes, halosilanes, haloethenes, and haloallenes,[2−4] and such trends can be expected when substituents are electronegative. A more interesting and subtler question is whether the halogen substitution is additive, i.e., whether each new substituent reduces enthalpy by equal amount. The inspection of Tables 2 and 3 reveals that it does not. Halomethanes, in particular show strong nonadditivity, i.e., tetrahalo derivative does not show 4-fold decrease in enthalpy with respect to methane. The possible explanation for this behavior was discussed previously.[2] The small, but observable, nonadditivity in substituent effects can be attributed to the fact that halogen substituents do not interact with the parent molecular fragment in exclusively inductive way (i.e., resonance or steric effects play a secondary role).

Table 3. The Reduction in Enthalpy upon Halogenation in Derivatives of Methane, Ethene, and Allene vs Parent Hydrocarbon.[1,4−6] When Isomers Exist, the Average Stabilization Energy of Corresponding Isomers Is Listed in the Table

no. and type of halogens	parent: CH_4	parent: C_2H_4	parent: C_3H_4
1F	164.7	194.0	165.6
2F	376.4	373.0	348.0
3F	618.3	549.0	536.8
4F	858.6	722.5	736.1
1Cl	9.1	26.1	10.7
2Cl	20.9	43.3	21.5
3Cl	28.6	56.7	33.4
4Cl	21.4	64.9	45.5

Conclusion

In this work we have used high-level computational method in order to probe substituent effects in halogenated heterocycles. In the absence of experimental data this appears to be the method of choice. The method has sufficient energy sensitivity to reveal interesting trends in relative isomer stabilities. The energy "resolution" in this approach is currently comparable (or better) than the experimentally achievable one and should stimulate further studies of substituent effects on compound thermochemistry.

Supporting Information Available: Geometries and computed total energies. This material is available free of charge via the Internet at http://www.acs.org.

JO0108010