J. Phys. Chem. A **2007,** *111,* 1713−1720

Energetics of C−F, C−Cl, C−Br, and C−I Bonds in 2-Haloethanols. Enthalpies of Formation of XCH_2CH_2OH (X = F, Cl, Br, I) Compounds and of the 2-Hydroxyethyl Radical

Carlos E. S. Bernardes and Manuel E. Minas da Piedade*

Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa,
1649-016 Lisboa, Portugal

Luísa M. P. F. Amaral, Ana I. M. C. L. Ferreira, and Manuel A. V. Ribeiro da Silva

Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do
Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal

Hermínio P. Diogo

Centro de Química Estrutural, Complexo Interdisciplinar, Instituto Superior Técnico,
1049-001 Lisboa, Portugal

Benedito J. Costa Cabral

Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1649-016 Lisboa,
Portugal, and Grupo de Física Matemática da Universidade de Lisboa, Av. Professor Gama Pinto 2,
1649-003 Lisboa, Portugal

Received: November 15, 2006; In Final Form: December 18, 2006

The energetics of the C−F, C−Cl, C−Br, and C−I bonds in 2-haloethanols was investigated by using a combination of experimental and theoretical methods. The standard molar enthalpies of formation of 2-chloro-, 2-bromo-, and 2-iodoethanol, at 298.15 K, were determined as $\Delta_f H_m^o(ClCH_2CH_2OH, l) = -315.5 \pm 0.7$ kJ·mol^{-1}, $\Delta_f H_m^o(BrCH_2CH_2OH, l) = -275.8 \pm 0.6$ kJ·mol^{-1}, $\Delta_f H_m^o(ICH_2CH_2OH, l) = -207.3 \pm 0.7$ kJ·mol^{-1}, by rotating-bomb combustion calorimetry. The corresponding standard molar enthalpies of vaporization, $\Delta_{vap} H_m^o(ClCH_2CH_2OH) = 48.32 \pm 0.37$ kJ·mol^{-1}, $\Delta_{vap} H_m^o(BrCH_2CH_2OH) = 54.08 \pm 0.40$ kJ·mol^{-1}, and $\Delta_{vap} H_m^o(ICH_2CH_2OH) = 57.03 \pm 0.20$ kJ·mol^{-1} were also obtained by Calvet-drop microcalorimetry. The condensed phase and vaporization enthalpy data lead to $\Delta_f H_m^o(ClCH_2CH_2OH, g) = -267.2 \pm 0.8$ kJ·mol^{-1}, $\Delta_f H_m^o(BrCH_2CH_2OH, g) = -221.7 \pm 0.7$ kJ·mol^{-1}, and $\Delta_f H_m^o(ICH_2CH_2OH, g) = -150.3 \pm 0.7$ kJ·mol^{-1}. These values, together with the enthalpy of selected isodesmic and isogyric gas-phase reactions predicted by density functional theory (B3LYP/cc-pVTZ) and CBS-QB3 calculations were used to derive the enthalpies of formation of gaseous 2-fluoroethanol, $\Delta_f H_m^o(FCH_2CH_2OH, g) = -423.6 \pm 5.0$ kJ·mol^{-1}, and of the 2-hydroxyethyl radical, $\Delta_f H_m^o(CH_2CH_2OH, g) = -28.7 \pm 8.0$ kJ·mol^{-1}. The obtained thermochemical data led to the following carbon−halogen bond dissociation enthalpies: $DH^o(X-CH_2CH_2OH) = 474.4 \pm 9.4$ kJ·mol^{-1} (X = F), 359.9 ± 8.0 kJ·mol^{-1} (X = Cl), 305.0 ± 8.0 kJ·mol^{-1} (X = Br), 228.7 ± 8.1 kJ·mol^{-1} (X = I). These values were compared with the corresponding C−X bond dissociation enthalpies in XCH_2COOH, XCH_3, XC_2H_5, $XCH{=}CH_2$, and XC_6H_5. In view of this comparison the computational methods mentioned above were also used to obtain $\Delta_f H_m^o(FCH_2COOH, g) = -594.0 \pm 5.0$ kJ·mol^{-1} from which $DH^o(F-CH_2COOH) = 435.4 \pm 5.4$ kJ·mol^{-1}. The order $DH^o(C-F) > DH^o(C-Cl) > DH^o(C-Br) > DH^o(C-I)$ is observed for the haloalcohols and all other RX compounds. It is finally concluded that the major qualitative trends exhibited by the C−X bond dissociation enthalpies for the series of compounds studied in this work can be predicted by Pauling's electrostatic-covalent model.

Introduction

The energetics of halogenated hydrocarbons and their derivatives has been a topic of considerable interest in recent years due, in particular, to the impact of chlorofluorocarbons (CFCs) in the depletion of stratospheric ozone.[1−3] To rationalize the mechanisms of these processes and the effectiveness of various possible palliative agents, a large body of reliable enthalpy of formation, $\Delta_f H_m^o$, and bond dissociation enthalpy, $DH^o(C-X)$ (X = F, Cl, Br, I), data is necessary.[4,5] A survey of some major databases[6−8] immediately reveals, however, that the available experimental $\Delta_f H_m^o$ and $DH^o(C-X)$ values for halogenated hydrocarbons are scarce, and frequently of poor accuracy, a situation that does not show a tendency for improvement because, currently, very few active laboratories around the world

---

* Corresponding author. E-mail: memp@fc.ul.pt.

10.1021/jp0675678 CCC: $37.00

have the equipment and the know-how to determine enthalpies of combustion of haloorganic compounds. This lack of data can, in principle, be supplemented by using empirical estimation schemes or quantum chemistry methods.[9] However, an accurate and as large as possible body of reliable experimental values including molecules with a variety of chemical structures and bond combinations is always required to evaluate the predictions of these methods and, in the case of empirical schemes, it is also needed to obtain the bond or group contributions used in the estimates.[9−11] This, and the fact that some haloethanols have recently been suggested as possible replacements for CFCs,[12,13] were among the reasons that prompted us to obtain the enthalpies of formation of 2-chloro, 2-bromo, and 2-iodoethanol in the liquid and gaseous states using combustion calorimetry and Calvet-drop vaporization calorimetry. These values, together with the enthalpy of selected isodesmic and isogyric gas-phase reactions predicted by density functional theory (B3LYP/cc-pVTZ) and the CBS-QB3 methods were then used to derive the enthalpy of formation of gaseous 2-fluoroethanol, which could not be experimentally obtained due to the lack of a sample with the high purity required by the calorimetric measurements.

Another motivation of this work concerns the influence of the OH group in the C−X bond dissociation enthalpy. Hence, the obtained $\Delta_f H^o_m$(XCH$_2$CH$_2$OH, g), together with B3LYP/cc-pVTZ and CBS-QB3 results for the enthalpies of isodesmic and isogyric reactions (an isodesmic reaction is one in which the number of chemical bonds of each formal type, e.g., C−H and C=C, does not change, and in an isogyric reaction the number of electron pairs is also conserved[14]), were used to propose a value for the enthalpy of formation of the gaseous 1-hydroxyethyl radical, which is also relevant for combustion and atmospheric chemistry,[15,16] and whose reported experimental and predicted data span a range of 39.8 kJ·mol^{-1}.[8,17−22] Based on the selected value, it was possible to obtain the C−X bond dissociation enthalpies in 2-fluoro-, 2-chloro-, 2-bromo-, and 2-iodoethanol, and to compare the energetics of these bonds with the similar ones in XCH$_2$COOH, XCH$_3$, XC$_2$H$_5$, XCH$_2$Cl, XCH=CH$_2$, and XC$_6$H$_5$ compounds.

Materials and Methods

General Information. Refractive indexes relative to the sodium D line at 589 nm were measured at 293.15 K with a CETI Abbe type digital refractometer. GC−MS experiments were performed on an Agilent 6890 gas chromatograph coupled to an Agilent 5973N mass detector. The transfer line, ion source, and quadrupole analyzer were maintained at 553, 503, and 423 K, respectively. A TRB-5MS capillary column from Agilent (5% diphenyl/95% dimethylpolysiloxane; 30 m × 0.25 mm i.d., 0.25 μm d_f) was used. The carrier gas was helium maintained at a constant pressure of 1.19 bar. The temperature of the injector was set at 473 K and the oven temperature was programmed as follows: 373 K (3 min), ramp at 5 K·min^{-1}, 513 K (5 min). The ^{1}H NMR spectra were obtained at ambient temperature, in CDCl$_3$, on a Bruker Ultrashield 400 MHz spectrometer.

Materials. 2-Chloroethanol (Aldrich, 99%), 2-bromoethanol (Aldrich, 95%), and 2-iodoethanol (Aldrich, 99%) were distilled twice at 100 Pa and 308 K. The colorless liquids obtained were stored in the dark, inside Schlenk tubes under N$_2$ or Ar atmosphere prior to use. The analytical data obtained for the samples are as follows.

2-Chloroethanol: $n^{20} = 1.442 \pm 0.001$ (the uncertainty corresponds to the standard deviation of the mean of seven independent determinations). This result is in agreement with the value $n^{20} = 1.4419$[23] recommended in the literature. ^{1}H NMR (400 MHz, CDCl$_3$/TMS): $\delta = 3.832−3.869$ (m, 2-H), $\delta = 3.635−3.672$ (m, 2-H), and $\delta = 2.432−2.433$ (m, 1-H). The obtained ^{1}H NMR results are in accordance with those published in a reference database.[24] No impurities were detected by GC−MS.

2-Bromoethanol: $n^{20} = 1.491 \pm 0.003$ (the uncertainty corresponds to the standard deviation of the mean of seven independent determinations). This result is in agreement with the value $n^{20} = 1.4915$ recommended in the literature.[23] ^{1}H NMR (400 MHz, CDCl$_3$/TMS): $\delta = 3.892−3.928$ (m 4-H) and $\delta = 3.519−3.555$ (m 1-H). These results are in good agreement with those recommended in the literature.[24] No impurities were detected by GC−MS.

2-Iodoethanol: $n^{20} = 1.571 \pm 0.004$ (the uncertainty corresponds to the standard deviation of the mean of seven independent determinations). This result is in agreement with the value $n^{20} = 1.5713$[23] recommended in the literature. ^{1}H NMR (400 MHz, CDCl$_3$/TMS): $\delta = 3.768−3.813$ (m 4-H) and $\delta = 3.235−3.280$ (m 1-H). No impurities were detected by GC−MS.

Several attempts were made to obtain a fluoroethanol sample with the purity required by the calorimetric experiments, but GC−MS analysis of the purified samples always revealed impurity contents larger than 2%.

Combustion Calorimetry. The standard enthalpy of combustion of 2-chloroethanol was determined using the isoperibol rotating-bomb combustion calorimeter previously described. The bomb was platinum lined and had an internal volume of 0.337 dm^3.[25−27] The combustion experiments with 2-bromo- and 2-iodoethanol were performed in another isoperibol rotating-bomb combustion calorimeter with a platinum lined bomb of 0.258 dm^3 internal volume.[28−30] The energy equivalents of both calorimeters were determined, in the conventional way, without bomb rotation,[31−34] from the combustion of benzoic acid (NIST SRM 39i, BCS−CRM 190, or BCS−CRM 190r).

In the case of 2-chloroethanol a sample with a mass in the range 0.82727−1.00609 g was sealed in a Melinex bag (mass: 0.04774−0.06722 g) and placed in a platinum crucible together with 0.13990−0.20028 g of *n*-hexadecane (Aldrich, Gold Label) that served as a combustion auxiliary. The crucible was supported by a platinum ring inside the bomb. The total mass of the crucible and the ring was 11.7 g. A platinum wire of diameter 0.05 mm (Goodfellow, mass fraction: 0.9999) was fastened between the ignition electrodes. A cotton thread fuse of empirical formula CH$_{1.686}$O$_{0.843}$ (mass: 2.59−3.17 mg) was tied to the platinum wire. The sample, Melinex bag, *n*-hexadecane, fuse, crucible, and ring were weighed with a precision of $\pm 10^{-5}$ g in a Mettler AE 240 balance. The crucible was adjusted to the bomb head and the fuse was placed in contact with the sample, without touching the crucible walls. After the introduction of 20.00 cm^3 of a 0.09016 mol·dm^{-3} As$_2$O$_3$ aqueous solution inside the bomb, the bomb was closed and purged twice by charging it with oxygen at a pressure of 1.01 MPa and then venting the overpressure. The oxygen pressure inside the bomb was increased to 3.04 MPa and the bomb was transferred to the inside of the calorimeter proper. The electrical connections of the firing circuit were attached to the bomb head, and the calorimeter proper was filled with an amount of distilled water as close as possible to the average mass of water used in the calibration experiments (5217.0 g). The water added to the calorimeter proper in each experiment was weighed to ±0.1 g in a Mettler PC 8000 balance. Calorimeter temperatures were measured to $\pm 10^{-4}$ K using a Hewlett-Packard (HP2804A) quartz thermometer. The duration

TABLE 1: Energies and Enthalpies of Combustion, Enthalpies of Vaporization, and Enthalpies of Formation of 2-Chloro-, 2-Bromo-, and 2-Iodoethanol, at 298.15 K

compound	$-\Delta_c u^o$/J·g^{-1}	$-\Delta_c H_m^o$/kJ·mol^{-1}	$-\Delta_f H_m^o$(l)/kJ·mol^{-1}	$\Delta_{vap} H_m^o$/kJ·mol^{-1}	$-\Delta_f H_m^o$(g)/kJ·mol^{-1}
$ClCH_2CH_2OH$	15011.1 ± 1.9	1209.8 ± 0.6	315.5 ± 0.7	48.32 ± 0.37	267.2 ± 0.8
$BrCH_2CH_2OH$	9623.5 ± 1.4	1203.8 ± 0.5	275.8 ± 0.6	54.08 ± 0.40	221.7 ± 0.7
ICH_2CH_2OH	7515.6 ± 2.4	1294.3 ± 0.6	207.3 ± 0.7	57.03 ± 0.20	150.3 ± 0.7

of the fore, main, and after periods was 20 min each. Discharge of a 1400 μF capacitor through the platinum wire referred to above ignited the cotton thread fuse and subsequently the sample. For each experiment the ignition temperature was chosen so that the final temperature would be close to 298.15 K. The rotation of the bomb was started when the temperature rise of the main period reached about 0.63 of its total value and was continued throughout the experiment. It has been shown that by adopting this procedure, the frictional work due to the rotation of the bomb is automatically accounted for in the calculation of the adiabatic temperature rise.[35,36] The HNO_3 formed from traces of atmospheric N_2 remaining inside the bomb was analyzed by the Devarda's alloy method.[37]

The general procedures followed in the combustion of 2-bromo- and 2-iodoethanol were similar to those described for 2-chloroethanol. In the case of 2-bromoethanol 25.00 cm^3 of 0.09016 mol·dm^{-3} As_2O_3 aqueous solution were placed inside the bomb. The presence of the arsenious oxide solution insured that all X_2 (X = Cl, Br) formed in the combustion was reduced to aqueous HX.[38−40] Because mixtures of X_2 and HX of variable composition are always formed in the combustion of chlorine or bromine organic compounds this method enabled us to simplify the analysis of the final state.[38] In the experiments with 2-iodoethanol the bomb contained 10.00 cm^3 of a 0.9090 mol·dm^{-3} KI aqueous solution to achieve a quantitative conversion of the I_2 formed in the combustion to I_3^-(aq).[41] Although only elemental iodine is found in the combustion products of organoiodine compounds,[38] the use of the potassium iodide solution eliminates the uncertainty in the determination of the final state due to the distribution of I_2 among solid, aqueous, and gaseous phases.[41] The extent of the reactions of the elemental halogens formed in the combustions with the arsenious oxide or potassium iodide solutions were found by titrating the final bomb solutions with sodium thiosulphate (0.1000 mol·dm^{-3}).[37]

Calvet Drop Calorimetry. The enthalpies of vaporization of chloro-, bromo-, and iodoethanol were measured by using an electrically calibrated Calvet drop microcalorimeter previously described.[42,43] The samples with masses in the ranges 12.8−34.8 mg ($ClCH_2CH_2OH$), 20.4−35.3 mg ($BrCH_2CH_2OH$), and 20.8−47.2 mg (ICH_2CH_2OH), were weighed to 1 × 10^{-6} g inside a small glass capillary closed by Parafilm tape. The capillary was equilibrated at 298.15 K inside a furnace placed above the calorimetric cell for ca. 20 min, and dropped into the cell, under N_2 atmosphere, after removal of the Parafilm tape. The temperature of the cell was also 298.15 K. After dropping, the sample and reference cells were simultaneously evacuated to 0.13 Pa and the measuring curve corresponding to the evaporation of the sample was acquired. The enthalpy of vaporization of the sample was subsequently derived from the area of the obtained curve and the calibration constant of the apparatus. No decomposition residues were found inside the calorimetric cell at the end of the experiments. The accuracy of the method was previously checked by determining the standard molar enthalpy of vaporization of ethanol at 298.15 K. The obtained result $\Delta_{vap}H_m^o(C_2H_5OH) = 42.11 \pm 0.25$ kJ·mol^{-1} (the uncertainty quoted is twice the standard deviation of the mean of five determinations) is in good agreement with the value $\Delta_{vap}H_m^o(C_2H_5OH) = 42.46 \pm 0.12$ kJ·mol^{-1} [44] recommended in the literature.

Computational Details. Density functional theory (DFT) and complete basis set extrapolation procedures (CBS) were applied to predict thermochemical properties for the systems of interest. In DFT the total energies (E) are obtained from[45]

$$E = V_{NN} + H^{CORE} + V_{ee} + E_X[\rho] + E_C[\rho] \qquad (1)$$

where V_{NN} is the nuclear−nuclear interaction, H^{CORE} is a monoelectronic contribution to the total energy, including electron kinetic and electron−nuclear interaction energies, and V_{ee} is the Coulombic interaction between the electrons. The terms $E_X[\rho]$ and $E_C[\rho]$ represent the exchange and correlation contributions, which are functionals of the electron density ρ. DFT calculations were performed with the hybrid B3LYP exchange correlation functional, which is a combination of Becke's three-parameter functional (B3)[46] and the Lee, Yang, and Parr (LYP)[47] correlation functional. Although it is known that DFT methods systematically underestimate homolytic bond dissociation enthalpies,[48] application of DFT to the prediction of $DH°$ data through isodesmic/isogyric reactions, as done in the present work, may overcome these limitations. Full geometry optimizations have been carried out with the cc-pVTZ basis set.[49−51] Zero-point vibrational energies (ZPE's) and thermal energy (TE) contributions were taken into account in the calculation of the enthalpies of all species at 298.15 K. The obtained frequencies are harmonic and were not scaled. Empirical scaling factors are usually introduced to correct for deviations from (lower) experimental anharmonic frequencies. However, the scaling factors are dependent on the theoretical method and basis set combination. We have, therefore, assumed that the computed harmonic frequencies are sufficiently accurate to estimate the ZPE and TE corrections mentioned above.

Complete basis set extrapolation calculations of enthalpies of reaction were carried out with the CBS-QB3 composite method.[52,53] The importance of applying CBS procedures to the calculation of thermochemical properties is related to the fact that ab initio energies converge slowly with the basis set size.[48]

All the theoretical calculations were performed using the Gaussian-03 program.[54]

Results and Discussion

The 2005 IUPAC recommended standard atomic masses were used in the calculation of all molar quantities.[55]

Enthalpies of Formation and Vaporization of Chloro-, Bromo-, and Iodoethanol. Detailed results of the combustion calorimetric experiments are given as Supporting Information and lead to the standard massic energies of combustion ($\Delta_c u^o$) and the standard molar enthalpies of combustion ($\Delta_c H_m^o$) of 2-chloro-, 2-bromo-, and 2-iodoethanol, at 298.15 K, shown in Table 1. The standard state corrections (Washburn corrections) were derived as recommended in the literature for organic compounds containing chlorine,[56,57] bromine,[38,40] and iodine,[56] using the auxiliary data included in the Supporting Information. The uncertainties quoted for $\Delta_c u^o$ represent the standard deviation of the mean of six individual results and those of $\Delta_c H_m^o$ correspond to twice the overall standard deviation of the mean, and include the contributions from the calibration with

TABLE 2: Experimental and Computed (B3LYP/cc-pVTZ and CBS-QB3) Enthalpies of Reaction at 298.15 K (Data in kJ·mol^{-1})

reaction	B3LYP/cc-pVTZ	Δ^a	CBS-QB3	Δ^a	experimental
$ClCH_2CH_2OH(g) + CH_4(g) = CH_3Cl(g) + C_2H_5OH(g)$	19.1	5.4	23.2	1.3	24.5 ± 1.1
$ClCH_2CH_2OH(g) + C_2H_6(g) = C_2H_5Cl(g) + C_2H_5OH(g)$	2.2	1.5	2.6	1.1	3.7 ± 1.0
$ClCH_2CH_2OH(g) + CH_3Br(g) = BrCH_2CH_2OH(g) + CH_3Cl(g)$	2.1	−3.1	2.6	−3.6	−1.0 ± 1.6
$ClCH_2CH_2OH(g) + C_2H_5Br(g) = BrCH_2CH_2OH(g) + C_2H_5Cl(g)$	−0.1	−4.6	−0.5	−4.2	−4.7 ± 2.2
$ClCH_2CH_2OH(g) + CH_3COOH(g) = ClCH_2COOH(g) + C_2H_5OH(g)$	29.2	5.6	28.2	6.6	34.8 ± 2.8
$ClCH_2CH_2OH(g) + BrCH_2COOH(g) = ClCH_2COOH(g) + BrCH_2CH_2OH(g)$	−0.5	−0.6	−4.1	3.0	−1.1 ± 3.5
$BrCH_2CH_2OH(g) + CH_4(g) = CH_3Br(g) + C_2H_5OH(g)$	17.0	8.5	20.6	4.9	25.5 ± 1.4
$BrCH_2CH_2OH(g) + C_2H_6(g) = C_2H_5Br(g) + C_2H_5OH(g)$	2.3	6.1	3.1	5.3	8.4 ± 1.8
$BrCH_2CH_2OH(g) + CH_3COOH(g) = BrCH_2COOH(g) + C_2H_5OH(g)$	29.7	6.1	32.3	3.5	35.8 ± 4.1

[a] $\Delta = [\Delta_r H^o_m(\text{experimental}) - \Delta_r H^o_m(\text{calculated})]$.

TABLE 3: Computed Enthalpies of Reaction and Enthalpies of Formation of Gaseous Fluoroethanol and Fluoroacetic Acid at 298.15 K (Data in kJ·mol^{-1})

	B3LYP/cc-pVTZ		CBS-QB3	
reaction	$\Delta_r H^o_m$	$-\Delta_f H^o_m(g)$	$\Delta_r H^o_m$	$-\Delta_f H^o_m(g)$
fluoroethanol				
$FCH_2CH_2OH(g) + CH_2F_2(g) = CHF_3(g) + C_2H_5OH(g)$	−56.8	421.5 ± 2.9	−55.5	422.8 ± 2.9
$FCH_2CH_2OH(g) + PhCH_3(g) = PhCH_2F(g) + C_2H_5OH(g)$	9.2	421.2 ± 0.9	9.2	421.2 ± 0.9
$FCH_2CH_2OH(g) + C_6H_{12}(g) = C_6H_{11}F(g) + C_2H_5OH(g)$	−19.8	428.7 ± 1.4	−21.7	426.8 ± 1.4
fluoroacetic acid				
$FCH_2COOH(g) + CH_2F_2(g) = CHF_3(g) + CH_3COOH(g)$	−83.3	592.6 ± 3.8	−82.7	593.2 ± 3.8
$FCH_2COOH(g) + PhCH_3(g) = PhCH_2F(g) + CH_3COOH(g)$	−17.3	592.3 ± 2.7	−18.0	591.6 ± 2.7
$FCH_2COOH(g) + C_6H_{12}(g) = C_6H_{11}F(g) + CH_3COOH(g)$	−46.3	599.8 ± 2.8	−48.9	597.2 ± 2.8

benzoic acid, from the energy of combustion of Melinex, and from the *n*-hexadecane used as combustion auxiliary.[58,59] The $\Delta_c u^o$ and $\Delta_c H^o_m$ values refer to the reactions:

$$ClCH_2CH_2OH(l) + 2.5O_2(g) + 598H_2O(l) \rightarrow 2CO_2(g) + HCl{\cdot}600H_2O(l) \quad (2)$$

$$BrCH_2CH_2OH(l) + 2.5O_2(g) + 598\,H_2O(l) \rightarrow 2CO_2(g) + HBr{\cdot}600H_2O(l) \quad (3)$$

$$ICH_2CH_2OH(l) + 2.75O_2(g) \rightarrow 2CO_2(g) + 2.5H_2O(l) + 0.5I_2(cr) \quad (4)$$

and lead to the enthalpies of formation of the alcohols in the liquid state indicated in Table 1, by using $\Delta_f H^o_m(CO_2,\ g) = -393.51 \pm 0.13$ kJ·mol^{-1},[60] $\Delta_f H^o_m(H_2O,\ l) = -285.830 \pm 0.040$ kJ·mol^{-1},[60] $\Delta_f H^o_m(HCl{\cdot}600H_2O,\ l) = -166.540 \pm 0.005$ kJ·mol^{-1},[60,61] and $\Delta_f H^o_m(HBr{\cdot}600H_2O,\ l) = -120.924 \pm 0.005$ kJ·mol^{-1}.[61] Note that, according to normal combustion calorimetry practice, aqueous solutions containing 600 mol of H_2O per 1 mol of HCl or HBr were used as reference states for the halogenated products in eqs 2 and 3. Also indicated in Table 1 are the enthalpies of vaporization of the halogenated alcohols obtained by Calvet drop calorimetry, which together with the corresponding $\Delta_f H^o_m(l)$ lead to the enthalpies of formation of $ClCH_2CH_2OH$, $BrCH_2CH_2OH$, and ICH_2CH_2OH in the gaseous phase (Table 1).

To the best of our knowledge the enthalpies of combustion of 2-bromo- and 2-iodoethanol in the liquid state have never been determined, and the $\Delta_c H^o_m$ values reported for 2-chloroethanol[62,63] (which are not mentioned in major thermochemical compilations)[6,7,64] are essentially of historical value. In 1933 Popoff and Shirokich proposed $\Delta_c H^o_m(ClCH_2CH_2OH,\ l) = -1191.4 \pm 1.2$ kJ·mol^{-1} at 288 K, on the basis of four combustion experiments performed with a shaking bomb combustion calorimeter.[62] A decade later, using a rotating-bomb combustion calorimeter, Smith and Sunner reported $\Delta_c H^o_m(ClCH_2CH_2OH,\ l) = -1214.0 \pm 1.2$ kJ·mol^{-1} at 298.15 K, a value that is close to the result obtained in this work (Table 1), although not within the uncertainty interval. These authors also mention that the shaking bomb method used by Popoff and Shirokich tends to give less exothermic enthalpies of combustion for organochlorine compounds with high Cl content.[63]

In 1926, Matheus[65] reported $\Delta_{vap} H^o_m(ClCH_2CH_2OH) = 41.42 \pm 0.03$ kJ·mol^{-1} at 399.7 K. Conversion of this result to 298.15 K using $C^o_{p,m}(ClCH_2CH_2OH,\ l) = 142.5$ J·K^{-1} mol^{-1} [66] and $C^o_{p,m}(ClCH_2CH_2OH,\ g) = 74.8$ J·K^{-1} mol^{-1} (B3LYP/cc-pVTZ) leads to $\Delta_{vap} H^o_m(ClCH_2CH_2OH) = 48.3$ kJ·mol^{-1} in good agreement with the value obtained in this work. Finally, from the parameters of Antoine's equation reported by Stull,[7,67] to describe the vapor pressure of $ClCH_2CH_2OH$ in the range 269.0−401.9 K, it is possible to derive $\Delta_{vap} H^o_m(ClCH_2CH_2OH) = 45.4$ kJ·mol^{-1} at 298.15 K, which is 1.7 kJ·mol^{-1} lower than the result in Table 1.

The enthalpies of formation of $ClCH_2CH_2OH$ and $BrCH_2CH_2OH$ in Table 1, in conjunction with $\Delta_f H^o_m(CH_4,\ g) = -74.4 \pm 0.4$ kJ·mol^{-1},[6] $\Delta_f H^o_m(C_2H_6,\ g) = -83.8 \pm 0.3$ kJ·mol^{-1},[6] $\Delta_f H^o_m(C_2H_5OH,\ g) = -235.2 \pm 0.3$ kJ·mol^{-1},[6] $\Delta_f H^o_m(CH_3COOH,\ g) = -432.8 \pm 2.5$ kJ·mol^{-1},[6] $\Delta_f H^o_m(CH_3Cl,\ g) = -81.9 \pm 0.5$ kJ·mol^{-1},[6] $\Delta_f H^o_m(C_2H_5Cl,\ g) = -112.1 \pm 1.1$ kJ·mol^{-1},[6] $\Delta_f H^o_m(ClCH_2COOH,\ g) = -430.0 \pm 1.0$ kJ·mol^{-1},[68,69] $\Delta_f H^o_m(CH_3Br,\ g) = -35.4 \pm 1.1$ kJ·mol^{-1},[6] $\Delta_f H^o_m(C_2H_5Br,\ g) = -61.9 \pm 1.6$ kJ·mol^{-1},[6] and $\Delta_f H^o_m(BrCH_2COOH,\ g) = -383.5 \pm 3.1$ kJ·mol^{-1},[68,69] were used to calculate the enthalpies of the isodesmic and isogyric reactions in Table 2. Also indicated in that table are the corresponding values obtained by the B3LYP/cc-pVTZ and CBS-QB3 methods and the deviations $\Delta = [\Delta_r H^o_m(\text{experimental}) - \Delta_r H^o_m(\text{calculated})]$. These results are based on the gauche conformations of the haloalcohols (Figure 1) which, according to both methods, are the most stable, in agreement with results from infrared spectroscopy and electron diffraction studies.[70−78] It can be concluded that the computational chemistry methods used in

TABLE 4: Enthalpies of Isodesmic Reactions and Enthalpies of Formation of the 2-Hydroxyethyl Radical, at 298.15 K (Data in kJ·mol^{-1})

reaction	B3LYP/cc-pVTZ $\Delta_r H^o_m$	B3LYP/cc-pVTZ $\Delta_f H^o_m(CH_2CH_2OH)$	CBS-QB3 $\Delta_r H^o_m$	CBS-QB3 $\Delta_f H^o_m(CH_2CH_2OH)$
$C_2H_5OH(g) + C_2H_5(g) \rightarrow C_2H_6(g) + CH_2CH_2OH(g)$	2.2	−30.2 ± 2.0	3.9	−28.5 ± 2.0
$C_2H_5OH(g) + CH_3(g) \rightarrow CH_4(g) + CH_2CH_2OH(g)$	−17.7	−31.8 ± 0.6	−11.6	−25.7 ± 0.6
$C_3H_7OH(g) + CH_3(g) \rightarrow C_2H_6(g) + CH_2CH_2OH(g)$	−11.6	−36.2 ± 0.6	−1.1	−25.7 ± 0.6
$ClCH_2CH_2OH(g) + C_2H_5(g) \rightarrow ClC_2H_5(g) + CH_2CH_2OH(g)$	4.4	−31.7 ± 2.4	6.5	−29.6 ± 2.4
$ClCH_2CH_2OH(g) + CH_3(g) \rightarrow CH_3Cl\ (g) + CH_2CH_2OH(g)$	1.4	−37.2 ± 1.0	11.6	−27.0 ± 1.0
$BrCH_2CH_2OH(g) + C_2H_5(g) \rightarrow C_2H_5Br(g) + CH_2CH_2OH(g)$	4.5	−36.3 ± 2.7	7.0	−33.8 ± 2.7
$BrCH_2CH_2OH(g) + CH_3(g) \rightarrow CH_3Br(g) + CH_2CH_2OH(g)$	−0.7	−40.3 ± 1.3	9.0	−30.6 ± 1.3

this work reproduce the experimental $\Delta_r H^o_m$ data with average and maximum deviations of 2.8 kJ·mol^{-1} and 8.5 kJ·mol^{-1} (B3LYP/cc-pVTZ), and 3.7 kJ·mol^{-1} and 6.6 kJ·mol^{-1} (CBS-QB3), respectively. This supports the reliability of the theoretical results and indicates a good thermodynamic consistency between the standard enthalpy of formation data used to derive the experimental $\Delta_r H^o_m$ values in Table 2.

Based on the enthalpies of the isodesmic and isogyric reactions in Table 3 computed by the B3LYP/cc-pVTZ and CBS-QB3 methods and on $\Delta_f H^o_m(C_6H_5CH_3, g) = 50.5 \pm 0.5$ kJ·mol^{-1},[6] $\Delta_f H^o_m(C_6H_{12}, g) = -123.3 \pm 0.8$ kJ·mol^{-1},[6] $\Delta_f H^o_m(CH_2F_2, g) = -452.3 \pm 0.9$ kJ·mol^{-1},[6] $\Delta_f H^o_m(CHF_3, g) = -695.4 \pm 2.7$ kJ·mol^{-1},[6] $\Delta_f H^o_m(C_6H_5CH_2F, g) = -126.3 \pm 0.2$ kJ·mol^{-1},[79] and $\Delta_f H^o_m(C_6H_{11}F, g) = -336.6 \pm 1.1$ kJ·mol^{-1},[79] it was possible to derive the enthalpies of formation of gaseous fluoroethanol and fluoroacetic acid (Table 3). Fluoroacetic acid had not been included in our previous study of the energetics of haloacetic acids.[68] It is noted that the values of $\Delta_f H^o_m(FCH_2CH_2OH, g)$ and $\Delta_f H^o_m(FCH_2COOH, g)$ obtained from the various $\Delta_r H^o_m$ results and the corresponding auxiliary enthalpy of formation data are in good agreement, indicating again a very good thermodynamic consistency between the theoretical reaction enthalpies and the experimental standard enthalpy of formation data. The selected values for $\Delta_f H^o_m(FCH_2CH_2OH, g) = -423.6 \pm 5.0$ kJ·mol^{-1} and $\Delta_f H^o_m(FCH_2COOH, g) = -594.0 \pm 5.0$ kJ·mol^{-1} are averages of the CBS-QB3 results in Table 3 with an assumed uncertainty of 5.0 kJ·mol^{-1}. The enthalpy of formation of fluoroethanol refers to the gauche conformation, which, as in the case of the chloro and bromo derivatives, was found to be the most stable. This conclusion is also supported by published results of microwave spectroscopy, infrared spectroscopy, and electron diffraction studies.[71,80−82]

Enthalpy of Formation of the CH_2CH_2OH Radical and X−CH_2CH_2OH Bond Dissociation Enthalpies. The standard enthalpy of formation of the CH_2CH_2OH radical was estimated according to the following procedure. First, the enthalpy of the isodesmic and isogyric reactions in Table 4 ($\Delta_r H^o_m$) were computed by using the B3LYP/cc-pVTZ and CBS-QB3 methods. Second, $\Delta_f H^o_m(CH_2CH_2OH, g)$ was calculated from *each* theoretical result for those reaction enthalpies, by using the enthalpies of formation of the gaseous haloalcohols in Table 1 together with the enthalpies of formation of $CH_4(g)$, $C_2H_6(g)$, $C_2H_5OH(g)$, $CH_3Cl(g)$, $C_2H_5Cl(g)$, $CH_3Br(g)$, and $C_2H_5Br(g)$ indicated above and $\Delta_f H^o_m(C_3H_7OH, g) = -255.1 \pm 0.4$ kJ·mol^{-1},[6] $\Delta_f H^o_m(CH_3, g) = 146.7 \pm 0.3$ kJ·mol^{-1},[83] $\Delta_f H^o_m(C_2H_5, g) = 119 \pm 2$ kJ·mol^{-1}.[84] The uncertainties quoted for $\Delta_f H^o_m(CH_2CH_2OH)$ in Table 4 include only the contributions from the experimental data used in the calculations. It is noted in Table 3 that the B3LYP/cc-pVTZ predictions for the enthalpy of formation of CH_2CH_2OH are always slightly more negative (by 2−10 kJ·mol^{-1}) than found by the CBS-QB3 method. The mean results obtained by each method are $\Delta_f H^o_m(CH_2CH_2OH) = -34.8 \pm 2.8$ kJ·mol^{-1} (B3LYP/cc-pVTZ) and $\Delta_f H^o_m(CH_2CH_2OH) = -28.7 \pm 2.2$ kJ·mol^{-1} (CBS-QB3), where the assigned uncertainties represent twice the standard deviation of the mean. The latter value, which corresponds to the higher level theoretical method, with an assumed uncertainty of ±8.0 kJ·mol^{-1} was selected in this work. The previously reported experimental and theoretical enthalpies of formation of the 2-hydroxyethyl radical range from −16.7 to −56.5 kJ·mol^{-1}.[8,17−22] From mass spectrometry results, Takhistov proposed $\Delta_f H^o_m(CH_2CH_2OH) = -29.3$ kJ·mol^{-1}.[17] Appearance energy measurements by Holmes et al. led to $\Delta_f H^o_m(CH_2CH_2OH) = -56.5 \pm 12.6$ kJ·mol^{-1}.[18] Using the enthalpy of reaction $OH(g) + C_2H_4(g) = C_2H_4OH(g)$ reported by Fulle et al., $\Delta_r H^o_m = -125.2 \pm 6.0$ kJ·mol^{-1},[19] in conjunction with $\Delta_f H^o_m(OH, g) = 37.3 \pm 0.3$ kJ·mol^{-1} [83] and $\Delta_f H^o_m(C_2H_4, g) = 52.5 \pm 0.3$ kJ·mol^{-1}, it is possible to derive $\Delta_f H^o_m(CH_2CH_2OH) = -35.4 \pm 6.0$ kJ·mol^{-1}. On the basis of an assumed C−Br bond dissociation enthalpy in bromoethanol of 288.7 ± 8.4 kJ·mol^{-1} and on experimentally determined photoionization thresholds for ethanol and bromoethanol, Ruscic et al. proposed $\Delta_f H^o_m(CH_2CH_2OH) = -36.4 \pm 8.4$ kJ·mol^{-1}.[20] G2 theory calculations by Curtiss et al. led to $\Delta_f H^o_m(CH_2CH_2OH) = -24.7 \pm 8.4$ kJ·mol^{-1}.[22] Finally, Espinosa-Garcia estimated $\Delta_f H^o_m(CH_2CH_2OH) = -16.7 \pm 4.2$ kJ·mol^{-1} from the enthalpies of three isodesmic and one hydrogenation reaction involving the 2-hydroxyethyl radical calculated at the MP4SDTQ/6-311++G(2d,p)//MP2/6-31G(d,p), QCISD(T)/6-311+G(d,p)//MP2/6-31G(d,p), CCSD(T)/6-311++G(2d,p)//MP2/6-31G(d,p), and CCSD(T)/cc-pVTZ//MP2/6-31G(d,p) levels of theory. The value recommended in this work (−28.7 ± 8.0 kJ·mol^{-1}) agrees particularly well with those reported by Takhistov (−29.3 kJ·mol^{-1})[17] and Curtiss et al. (−24.7 ± 8.4 kJ·mol^{-1}).[22]

Our selections $\Delta_f H^o_m(CH_2CH_2OH, g) = -28.7 \pm 8.0$ kJ·mol^{-1} and $\Delta_f H^o_m(FCH_2CH_2OH, g) = -423.6 \pm 5.0$ kJ·mol^{-1}, together with the enthalpies of formation of F (79.38 ± 0.30 kJ·mol^{-1}),[60] Cl (121.301 ± 0.008 kJ·mol^{-1}),[60] Br (111.87 ± 0.12 kJ·mol^{-1}),[60] and I (106.76 ± 0.04 kJ·mol^{-1}),[60] and of the gaseous haloethanols in Table 1, yield the X−CH_2CH_2OH bond dissociation enthalpies at 298.15 K indicated in Table 5. Also listed in Table 5 is the value $DH^o(F-CH_2COOH) = 435.4 \pm$

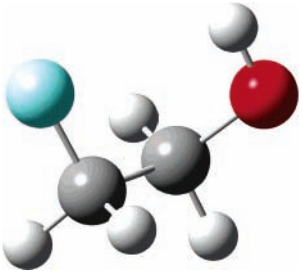


Figure 1. Gauche conformation of the haloalcohols XCH_2CH_2OH.

TABLE 5: R−X Bond Dissociation Enthalpies (Data in kJ·mol^{-1})

R	X = F	X = Cl	X = Br	X = I
CH_2CH_2OH	474.4 ± 9.4	359.9 ± 8.0	305.0 ± 8.0	228.7 ± 8.1
CH_2COOH	435.4 ± 5.4	313.3 ± 2.2	257.4 ± 3.7	202.1 ± 2.7
CH_3	463.5 ± 0.4	349.9 ± 0.6	294.0 ± 1.1	239.1 ± 1.4
C_2H_5	461.6 ± 2.1	352.4 ± 2.3	292.8 ± 2.6	233.9 ± 3.0
C_2H_3	517.8 ± 2.6	383.7 ± 3.1	332.3 ± 3.8	
C_6H_5	525.4 ± 3.7	399.4 ± 3.6	336.6 ± 5.3	272.0 ± 6.8

TABLE 6: Reorganization Energies Obtained by the B3LYP/cc-pVTZ Method (Data in kJ·mol^{-1})

precursor XR	X = F	X = Cl	X = Br
XC_6H_5	−3.2	−4.5	−4.4
$XCH{=}CH_2$	−7.3	−9.0	−8.6
XCH_2CH_2OH	−25.3	−24.1	−22.3
XCH_3	−27.9	−24.7	−22.6
XC_2H_5	−26.5	−24.2	−22.3
XCH_2COOH	−44.6	−45.4	−43.8

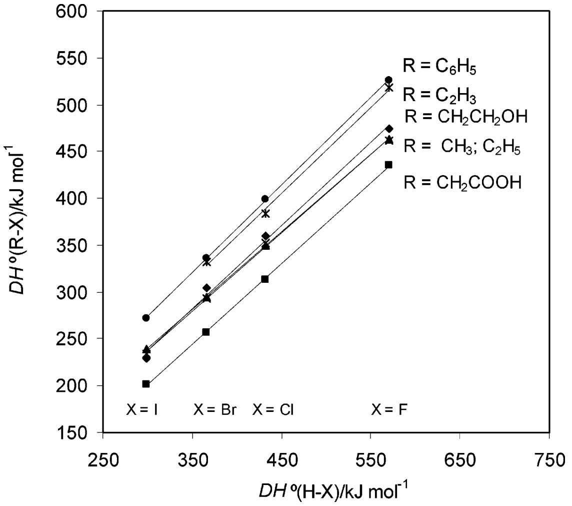
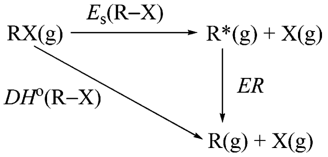


Figure 2. R−X bond dissociation enthalpies (from Table 5) versus the corresponding H−X bond dissociation enthalpies for X = F, Cl, Br, I and R = CH_2CH_2OH, CH_3, C_2H_5, C_2H_3, C_6H_5, and CH_2COOH.

SCHEME 1



5.4 kJ·mol^{-1} obtained from $\Delta_f H^o_m$(FCH$_2$COOH, g) = −594.0 ± 5.0 kJ·mol^{-1} proposed in this work and $\Delta_f H^o_m$(CH$_2$COOH, g) = −238.0 ± 2.0 kJ·mol^{-1},[68] together with C−X bond dissociation enthalpy data for other haloacetic acids and CH_3X, C_2H_5X, C_2H_3X, and C_6H_5X compounds. These were calculated from literature values cited above and $\Delta_f H^o_m$(CH$_3$F, g) = −237.4 kJ·mol^{-1} (estimated),[85] $\Delta_f H^o_m$(CH$_3$I, g) = 14.4 ± 1.4 kJ·mol^{-1},[6] $\Delta_f H^o_m$(C$_2$H$_5$F, g) = −263.2 ± 1.6 kJ·mol^{-1} (estimated),[86] $\Delta_f H^o_m$(C$_2$H$_5$I, g) = −8.1 ± 2.2 kJ·mol^{-1},[6] $\Delta_f H^o_m$(CH$_2$CH, g) = 299.6 ± 3.3 kJ·mol^{-1},[87] $\Delta_f H^o_m$(CH$_2$CHF, g) = −138.8 ± 1.7 kJ·mol^{-1},[6] $\Delta_f H^o_m$(CH$_2$CHCl, g) = 37.2 ± 1.2 kJ·mol^{-1},[6] $\Delta_f H^o_m$(CH$_2$CHBr, g) = 79.2 ± 1.9 kJ·mol^{-1},[6] $\Delta_f H^o_m$(C$_6$H$_5$, g) = 330.1 ± 3.4 kJ·mol^{-1},[87] $\Delta_f H^o_m$(C$_6$H$_5$F, g) = −115.9 ± 1.4 kJ·mol^{-1},[6] $\Delta_f H^o_m$(C$_6$H$_5$Cl, g) = 52.0 ± 1.3 kJ·mol^{-1},[6] $\Delta_f H^o_m$(C$_6$H$_5$Br, g) = 105.5 ± 4.1 kJ·mol^{-1},[6] $\Delta_f H^o_m$(C$_6$H$_5$I, g) = 164.9 ± 5.9 kJ·mol^{-1},[6] and $\Delta_f H^o_m$(ICH$_2$COOH, g) = −333.3 ± 1.8 kJ·mol^{-1}.[68,69]

Plots of *DH*°(R−X) versus *DH*°(H−X) (X = F, Cl, Br, I; R = CH_2CH_2OH, CH_3, C_2H_5, C_2H_3, C_6H_5, and CH_2COOH), obtained from the *DH*°(R−X) data in Table 5 and *DH*°(H−F) = 570.7 ± 0.8 kJ·mol^{-1}, *DH*°(H−Cl) = 431.6 ± 0.1 kJ·mol^{-1}, *DH*°(H−Br) = 366.2 ± 0.2 kJ·mol^{-1}, and *DH*°(H−I) = 298.3 ± 0.1 kJ·mol^{-1}, calculated from literature data,[60] are indicated in Figure 2. The various lines have similar slopes (0.89 for R = CH_2CH_2OH, 0.86 for R = CH_2COOH, 0.82 for R = CH_3, 0.84 for R = C_2H_5, 0.92 for R = C_2H_3, and 0.93 for R = C_6H_5) and correlation coefficients higher than 0.99. This type of representation has been previously used by us to discuss the C−Cl, C−Br, and C−I bonding energetics in several RX molecules.[68] As noted before, the decrease of *DH*°(R−X) from R = C_2H_3 and C_6H_5 to R = CH_3 and C_2H_5 reflects the change in hybridization of the carbon involved in the formation of the R−X bond. The sp^2 carbons forming the X−C_2H_3 and X−C_6H_5 bonds have a higher s character than the sp^3 carbons involved in the X−CH_3 and X−C_2H_5 bonds, and it is well-known that C−X bond dissociation enthalpies increase with increasing carbon s character.[88] As seen in Figure 2, the inclusion of the fluorine derivatives studied in this work in the correlations does not change these general conclusions. The line corresponding to the haloethanols is close to those for the haloalkanes, which also refer to the breaking of a C(sp^3)−X bond. The fact that the *DH*°(R−X) values for fluoro-, chloro-, and bromoethanol are larger by ca. 10 kJ·mol^{-1} than the corresponding values for R = CH_3 and C_2H_5, may reflect the gauche interaction X---H−O present in the former molecules, for which enthalpies in the range 1−10 kJ·mol^{-1} have been reported.[71−75,77,78,81] An inverse trend is apparently observed for iodoethanol, although this conclusion is somewhat hampered by the uncertainty intervals of the *DH*°(R−I) values. These findings are not unexpected because evidence from vibrational spectroscopy and electron diffraction experiments indicates that the "strength" of the gauche interaction in the haloethanols decreases along the series F > Cl > Br > I.[71,76,78]

We previously speculated that the additional decrease of *DH*°(X−R) from R = CH_3 and C_2H_5 to R = CH_2COOH was possibly due to the fact that the formation of the carboxymethyl radical upon breaking of the C−X bond might involve a larger reorganization energy than the formation of the methyl or ethyl radicals.[68] This view is supported in this work by the results of the calculations of the electronic reorganization energies, ER, defined in Scheme 1, at the B3LYP/cc-pVTZ level of theory (Table 6). In that scheme R* represents a fragment retaining the geometry of the precursor RX molecule, R is the relaxed radical resulting from the cleavage of the R−X bond, and E_s(R−X) is the "intrinsic" bond strength. As shown in Table 6, the relaxation energy of the carboxymethyl radical is indeed significantly larger than those of the methyl, ethyl, and 2-hydroxyethyl radicals.

Finally, as we previously noted for XCH_3, XC_2H_5, XC_2H_3, XC_6H_5, and XCH_2COOH compounds (X = Cl, Br, I) the trends exhibited by the X−CH_2CH_2OH bond dissociation enthalpies are also well described by Pauling's electrostatic-covalent model.[68] Based on Pauling's arithmetic mean expression,[89] it is possible to derive[68]

$$DH^o(\mathrm{R{-}X}) = DH^o(\mathrm{H{-}X}) + \frac{DH^o(\mathrm{R{-}R}) - DH^o(\mathrm{H{-}H})}{2} + 96.232[(\chi_R - \chi_X)^2 - (\chi_H - \chi_X)^2] \quad (5)$$

where in this case R = CH_2CH_2OH, X = F, Cl, Br, I, and χ_H, χ_X, and χ_R are the electronegativities of H, X and R, respectively.

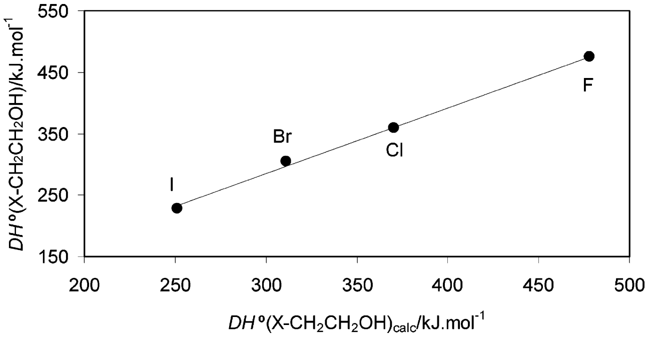


Figure 3. Experimental $DH°(X-CH_2CH_2OH)$ versus the corresponding values calculated from eq 6, $DH°(X-CH_2CH_2OH)_{calc}$, for X = F, Cl, Br, and I.

As shown in Figure 3, there is a good linear correlation between the experimental $DH^o(X-CH_2CH_2OH)$ values indicated above and the corresponding $DH^o(X-CH_2CH_2OH)_{calc}$ values calculated from eq 5, by using $DH^o(H-H) = 435.996 \pm 0.008$ kJ·mol^{-1}, $DH^o(HOCH_2CH_2-CH_2CH_2OH) = 371.5 \pm 11.8$ kJ·mol^{-1},[90] $\chi_H = 2.25$,[91] $\chi_F = 3.91$,[91] $\chi_{Cl} = 3.10$,[91] $\chi_{Br} = 2.95$,[91] $\chi_I = 2.74$,[91] and $\chi_{CH_2}CH_2OH = 2.45$.[92] The line in Figure 3 corresponds to the equation

$$DH^o(X-CH_2CH_2OH) = (1.065 \pm 0.039)DH^o(X-CH_2CH_2OH)_{calc} - (33.495 \pm 14.046) \quad (6)$$

with a regression coefficient of 0.999. The average and maximum errors in the estimation of $DH^o(X-CH_2CH_2OH)$ from eq 6 are 11 and 23 kJ·mol^{-1}, respectively

Acknowledgment. This work was supported by Fundação para a Ciência e a Tecnologia (FCT). Ph.D. grants from FCT are gratefully acknowledged by C.E.S.B (SFRH/BD/12329/2003) and L.M.P.F.A. (SFRH/BD/6719/2001). Thanks are also due to the European Social Fund (ESF), under the third Community Support Framework (CSF), for the award of a postdoctoral fellowship to L.M.P.F.A. (SFRH/BPD/25490/2005).

Supporting Information Available: Table S1 with a list of auxiliary thermochemical data. Details of the combustion calorimetric experiments including Tables S2−S4 with the results of all individual runs carried out on the haloalcohols. Table S5 with specific heat capacities, densities, and $-(\delta u/\delta p)_T$ for the haloethanol compounds and auxiliaries. Table S6 with the electronic energies, thermal corrections, zero point energies and enthalpies at 298.15 K for all the species studied by the B3LYP/cc-pVTZ and CBS-QB3 methods. Table S7 with the electronic energies of the R and R* species obtained by the B3LYP/cc-pVTZ method, and used to calculate the reorganization energies of R*. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Crutzen, P. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1758−1777.

(2) Molina, M. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1778−1785.

(3) Rowland, F. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1786−1798.

(4) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(5) Molina, M. J.; Molina, L. T.; Golden, D. M. *J. Phys. Chem.* **1996**, *100*, 12888−12896.

(6) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994.

(7) *NIST Chemistry WebBook*; NIST Standard Reference Database 69; National Institute of Standards and Technology: Gaithersburg, 2005; http://webbook.nist.gov/chemistry.

(8) Luo, Y. R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, FL, 2003.

(9) Irikura, K. K.; Frurip, D. J. *Computational Thermochemistry. Prediction and Estimation of Molecular Thermodynamics*; ACS Symposium Series No. 677; American Chemical Society: Washington, DC, 1998.

(10) *Computational Chemistry Comparison and Benchmark DataBase*; NIST Standard Reference Database 101; National Institute of Standards and Technology: Gaithersburg, MD, 2005; http://srdata.nist.gov/cccbdb/.

(11) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419−2438.

(12) Rajakumar, B.; Reddy, K. P. J.; Arunan, E. *J. Phys. Chem. A* **2003**, *107*, 9782−9793.

(13) Sellevåg, S. R.; Nielsen, C. J.; Søvde, O. A.; Myhre, G.; Sundet, J. K.; Stordal, F.; Isaksen, I. S. A. *Atmos. Environ.* **2004**, *38*, 6725−6735.

(14) Irikura, K. K. In *Extracting Thermochemical Information from Ab Initio Data* In *Energetics of Stable Molecules and Reactive Intermediates*; NATO-ASI Series C: Mathematical and Physical Sciences; Minas da Piedade, M. E., Ed.; Kluwer: Dordrecht, The Netherlands, 1999; Vol. 535.

(15) Tully, F. P. *Chem. Phys. Lett.* **1983**, *96*, 148−153.

(16) Tully, F. P. *Chem. Phys. Lett.* **1988**, *143*, 510−514.

(17) Takhistov, V. V. *Organic Mass Spectrometry*; Nauka: Leningrad, 1990.

(18) Holmes, J. L.; Lossing, F. P.; Mayer, P. M. *J. Am. Chem. Soc.* **1991**, *113*, 9723−9728.

(19) Fulle, D.; Hamann, H. F.; Hippler, H.; Jansch, C. P. *Ber. Bunsenges. Phys. Chem.* **1997**, *101*, 1433−1442.

(20) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1994**, *101*, 10936−10946.

(21) Espinosa-Garcia, J. *Chem. Phys. Lett.* **1997**, *278*, 209−212.

(22) Curtiss, L. A.; Lucas, D. J.; Pople, J. A. *J. Chem. Phys.* **1995**, *102*, 3292−3300.

(23) Lide, D. R. *Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 2005.

(24) *Spectral Data Base for Organic Compounds (SDBS)*; National Institute of Advanced Industrial Science and Technology (AIST): Japan, 2005; http://www.aist.go.jp/RIODB.

(25) Cox, J. D.; Gundry, H. A.; Head, A. J. *Trans. Faraday Soc.* **1964**, *60*, 653−665.

(26) Gundry, H. A.; Head, A. J. *J. Chem. Thermodyn.* **1978**, *10*, 195−200.

(27) Ribeiro da Silva, M. A. V.; Santos, L. M. N. B. F.; Schroder, B.; Dietze, F.; Beyer, L. *J. Chem. Thermodyn.* **2004**, *36*, 491−495.

(28) Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Lopes, A. J. M. *J. Chem. Thermodyn.* **1993**, *25*, 229−235.

(29) Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Jiye, F. *J. Chem. Thermodyn.* **1994**, *26*, 839−846.

(30) Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Alves da Silva, A. M. R. O. *J. Chem. Thermodyn.* **1995**, *27*, 633−641.

(31) Jessup, R. S. *J. Res. Natl. Bur. Stand.* **1942**, *29*, 247−270.

(32) Coops, J.; Jessup, R. S.; van Nes, K. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 3.

(33) Mosselman, C.; Churney, K. L. In *Experimental Chemical Thermodynamics*; Sunner, S., Månsson, M., Eds.; Pergamon Press: London, 1979; Vol. 1, pp 35−55.

(34) Marsh, K. N. *Recommended Reference Materials for the Realization of Physicochemical Properties*; IUPAC−Blackwell Scientific Publications: Oxford, U.K., 1987.

(35) Good, W. D.; Scott, D. W.; Waddington, G. *J. Phys. Chem.* **1956**, *60*, 1080−1089.

(36) Gunn, S. R. *J. Chem. Thermodyn.* **1971**, *3*, 19−34.

(37) Vogel, A. I.; Jeffery, G. H.; Bassett, J.; Mendham, J.; Denney, R. C. *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed.; Longman Scientific & Technical: London, 1991.

(38) Smith, L.; Hubbard, W. N. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, pp 181−204.

(39) Bjellerup, L. In *Experimental Thermochemistry*; Skinner, H. A., Ed.; Interscience: New York, 1962; Vol. 2, pp 41−56.

(40) Smith, L.; Bjellerup, L. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, pp 205−220.

(41) Carson, A. S.; Laye, P. G.; Pedley, J. B.; Welsby, A. M. *J. Chem. Thermodyn.* **1993**, *25*, 262−269.

(42) Kiyobayashi, T.; Minas da Piedade, M. E. *J. Chem. Thermodyn.* **2001**, *33*, 11−21.

(43) Bernardes, C. E. S.; Santos, L. M. N. B. F.; Minas da Piedade, M. E. *Meas. Sci. Technol.* **2006**, *17*, 1405−1408.

(44) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds*; IUPAC−Blackwell Scientific Publications: Oxford, 1985.

(45) Koch, W.; Holthausen, M. C. A. *Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley-VCH: Weinheim, 2002.

(46) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(47) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(48) Costa Cabral, B. J.; Canuto, S. *Chem. Phys. Lett.* **2005**, *406*, 300−305.

(49) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(50) Wilson, A. K.; Woon, D. E.; Peterson, K. A.; Dunning, T. H. *J. Chem. Phys.* **1999**, *110*, 7667−7676.

(51) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358−1371.

(52) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822−2827.

(53) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532−6542.

(54) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(55) Wieser, M. E. *Pure Appl. Chem.* **2006**, *78*, 2051−2066.

(56) Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 5.

(57) Hu, A. T.; Sinke, G. C.; Månsson, M.; Ringnér, B. *J. Chem. Thermodyn.* **1972**, *4*, 283−299.

(58) Bjellerup, L. *Acta Chem. Scand.* **1961**, *15*, 121−140.

(59) Olofsson, G. *Assignment of Uncertainties* In *Experimental Chemical Thermodynamics*; Sunner, S., Mansson, M., Eds.; Pergamon Press: Oxford, U.K., 1979; Vol. 1, pp 137−159.

(60) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *Codata Key Values for Thermodynamics*; Hemisphere: New York, 1989.

(61) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS Tables of Chemical Thermodynamics Properties. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. No. 2.

(62) Popoff, M. M.; Shirokich, P. K. *Z. Phys. Chem. (Leipzig)* **1933**, *167*, 183−187.

(63) Smith, L.; Sunner, S. *The Svedberg (Mem. Vol.)* **1944**, 352−369; *Chem. Abstr.* **1945**, *39*, 1100.

(64) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.

(65) Matheus, J. H. *J. Am. Chem. Soc.* **1926**, *48*, 562−576.

(66) Estimated, from bond additivity contributions based on the heat capacity data for liquid C_2H_5Cl, C_2H_5OH, C_3H_7OH, and C_5H_{12} given in: Domalski, E. S.; Hearing, E. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1−547.

(67) Stull, D. R. *Ind. Eng. Chem.* **1947**, *39*, 517−540.

(68) Lagoa, A. L. C.; Diogo, H. P.; Dias, M. P.; Minas da Piedade, M. E.; Amaral, L. M. P. F.; Ribeiro da Silva, M. A. V.; Martinho Simões, J. A.; Guedes, R. C.; Costa Cabral, B. J.; Schwarz, K.; Epple, M. *Chem. Eur. J.* **2001**, *7*, 483−489.

(69) Aleixo, A. I.; Oliveira, P. H.; Diogo, H. P.; Minas da Piedade, M. E. *Thermochim. Acta* **2005**, *428*, 131−136.

(70) Yamaha, M. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 865−871.

(71) Krueger, P. J.; Mettee, H. D. *Can. J. Chem.* **1964**, *42*, 326−339.

(72) Buckley, P.; Giguere, P. A.; Schneide, M. *Can. J. Chem.* **1969**, *47*, 901−910.

(73) Kastha, G. S.; Roy, S. B.; Nandy, S. K. *Ind. J. Phys.* **1972**, *46*, 293−299.

(74) Almenningen, A.; Fernholt, L.; Kveseth, K. *Acta Chem. Scand. A* **1977**, *31*, 297−305.

(75) Davenport, D.; Schwartz, M. *J. Mol. Struct.* **1978**, *50*, 259−266.

(76) Thomassen, H.; Samdal, S.; Hedberg, K. *J. Phys. Chem.* **1993**, *97*, 4004−4010.

(77) Durig, J. R.; Zhou, L.; Gounev, T. K.; Klaeboe, P.; Guirgis, G. A.; Wang, L. F. *J. Mol. Struct.* **1996**, *385*, 7−21.

(78) Durig, J. R.; Shen, S.; Guirgis, G. A. *J. Mol. Struct.* **2001**, *560*, 295−314.

(79) Schaffer, F.; Verevkin, S. P.; Rieger, H.-J.; Beckhaus, H.-D.; Rüchardt, C. *Liebigs Ann.* **1997**, 1333−1344.

(80) Igarashi, M.; Yamaha, M. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 871−876.

(81) Durig, J. R.; Klaeboe, P.; Guirgis, G. A.; Wang, L. F.; Liu, J. *Z. Phys. Chem.* **1995**, *191*, 23−45.

(82) Buckton, K. S.; Azrak, R. G. *J. Chem. Phys.* **1970**, *52*, 5652−5655.

(83) Ruscic, B.; Boggs, J. E.; Burcat, A.; Császár, A. G.; Demaison, J.; Janoschek, R.; Martin, J. M. L.; Morton, M. L.; Rossi, M. J.; Stanton, J. F.; Szalay, P. G.; Westmoreland, P. R.; Zabel, F.; Bérces, T. *J. Phys. Chem. Ref. Data* **2005**, *34*, 573−656.

(84) Tsang, W. Heats of Formation of Organic Free Radicals by Kinetic Methods. In *Energetics of Organic Free Radicals*; Martinho Simões, J. A., Greenberg, A., Liebman, J. F., Eds.; Blackie: London, 1996; pp 22−58.

(85) Parthiban, S.; de Oliveira, G.; Martin, J. M. L. *J. Phys. Chem. A* **2001**, *105*, 895−904.

(86) Tsang, W.; Hampson, R. F. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1087−1279.

(87) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744−2765.

(88) Coulson, C. A. *Valence*, 2nd ed.; Academic Press: New York, 1961; p 208−211.

(89) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960; p 92.

(90) Estimated from the enthalpy of formation of the radical $CH_2CH_2OH(g)$ selected in this work (-28.6 ± 8.0 kJ.mol^{-1}) and the enthalpy of formation of $HOCH_2CH_2CH_2CH_2OH(g)$ (-428.7 ± 6.5 kJ.mol^{-1}) given in ref 6.

(91) Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 34−41.

(92) The electronegativity of the CH_2CH_2OH group was calculated in this work by the method described in: Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 223−227.