# Energetics of C–Cl, C–Br, and C–I Bonds in Haloacetic Acids: Enthalpies of Formation of $XCH_2COOH$ (X = Cl, Br, I) Compounds and the Carboxymethyl Radical

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**Abstract:** The standard molar enthalpies of formation of chloro-, bromo-, and iodoacetic acids in the crystalline state, at 298.15 K, were determined as $\Delta_f H^\circ_m(C_2H_3O_2Cl,\ \text{cr}\ \alpha) = -(509.74 \pm 0.49)\ \text{kJ mol}^{-1}$, $\Delta_f H^\circ_m(C_2H_3O_2Br,\ \text{cr I}) = -(466.98 \pm 1.08)\ \text{kJ mol}^{-1}$, and $\Delta_f H^\circ_m\ (C_2H_3O_2I,\ \text{cr}) = -(415.44 \pm 1.53)\ \text{kJ mol}^{-1}$, respectively, by rotating-bomb combustion calorimetry. Vapor pressure versus temperature measurements by the Knudsen effusion method led to $\Delta_{sub} H^\circ_m(C_2H_3O_2Cl) = (82.19 \pm 0.92)\ \text{kJ mol}^{-1}$, $\Delta_{sub} H^\circ_m(C_2H_3O_2Br) = (83.50 \pm 2.95)\ \text{kJ mol}^{-1}$, and $\Delta_{sub} H^\circ_m(C_2H_3O_2I) = (86.47 \pm 1.02)\ \text{kJ mol}^{-1}$, at 298.15 K. From the obtained $\Delta_f H^\circ_m(\text{cr})$ and $\Delta_{sub} H^\circ_m$ values it was possible to derive $\Delta_f H^\circ_m(C_2H_3O_2Cl,\ \text{g}) = -(427.55 \pm 1.04)\ \text{kJ mol}^{-1}$, $\Delta_f H^\circ_m\ (C_2H_3O_2Br,\ \text{g}) = -(383.48 \pm 3.14)\ \text{kJ mol}^{-1}$, and $\Delta_f H^\circ_m(C_2H_3O_2I,\ \text{g}) = -(328.97 \pm 1.84)\ \text{kJ mol}^{-1}$. These data, taken with a published value of the enthalpy of formation of acetic acid, and the enthalpy of formation of the carboxymethyl radical, $\Delta_f H^\circ_m(CH_2COOH,\ \text{g}) = -(238 \pm 2)\ \text{kJ mol}^{-1}$, obtained from density functional theory calculations, led to $DH^\circ(H-CH_2COOH) = (412.8 \pm 3.2)\ \text{kJ mol}^{-1}$, $DH^\circ(Cl-CH_2COOH) = (310.9 \pm 2.2)\ \text{kJ mol}^{-1}$, $DH^\circ(Br-CH_2COOH) = (257.4 \pm 3.7)\ \text{kJ mol}^{-1}$, and $DH^\circ(I-CH_2COOH) = (197.8 \pm 2.7)\ \text{kJ mol}^{-1}$. A discussion of the C–X bonding energetics in $XCH_2COOH$, $CH_3X$, $C_2H_5X$, $C_2H_3X$, and $C_6H_5X$ (X = H, Cl, Br, I) compounds is presented.

**Keywords:** bond disssociation enthalpy · density functional calculations · haloacetic acids · heats of formation · thermochemistry

## Introduction

The considerable importance of chloro-, bromo-, and iodoacetic acids in organic synthesis is mainly associated with reactions involving the cleavage of the carbon–halogen bonds.[1] The ease of substitution of the halogen atoms is also the major factor in the industrial applications of the haloacetic acids.[2] Chloroacetic acid is the most industrially significant of the three. It is used, for example, in the manufacture of carboxymethyl celulose, carboxymethyl starch, and herbi-

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author: Vapor pressures of chloro-, bromo-, and iodoacetic acids as a function of temperature; detailed results of the combustion experiments on chloro-, bromo-, and iodoacetic acids; auxiliary enthalpy of formation data used in the calculations; total energies (hartrees) of the species involved in reaction (8) from DFT calculations.

cides.[2] Surprisingly, the available data on the energetics of these compounds are very scarce and, in particular, no information exists on the carbon–halogen "bond strengths". Only the enthalpy of formation of chloroacetic acid in the crystalline state has been determined,[3] and the measurement was made by static bomb combustion calorimetry which, in principle, does not yield reliable results for chlorine-containing organic compounds.[4] Other available data such as proton affinities,[5] gas-phase basicities,[5] and acidities in solution,[6] are essentially related to the –COOH group. This led us to determine the C–Cl, C–Br, and C–I bond dissociation enthalpies in the chloro-, bromo-, and iodoacetic acids by combining the results of rotating-bomb combustion calorimetry, heat capacity, and Knudsen effusion measurements, with data from density functional theory calculations.

## Results and Discussion

**Heat capacities and enthalpies of fusion**: Differential scanning calorimetry (DSC) measurements of the heat capacities of chloro-, bromo-, and iodoacetic acids in the crystalline state, at 298.15 K, led to: $C^{o}_{p,\mathrm{m}}(\mathrm{C_2H_3O_2Cl,\ cr}) = (106.7 \pm 2.0)\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $C^{o}_{p,\mathrm{m}}(\mathrm{C_2H_3O_2Br,\ cr}) = (107.4 \pm 1.2)\ \mathrm{J\,K^{-1}\,mol^{-1}}$, and $C^{o}_{p,\mathrm{m}}(\mathrm{C_2H_3O_2I,\ cr}) = (119.2 \pm 2.7)\ \mathrm{J\,K^{-1}\,mol^{-1}}$. The uncertainties quoted represent twice the mean deviation of three independent determinations. The corresponding gas phase heat capacities were derived from density functional theory calculations using the B3LYP/6-311 + G(d,p) level of theory in the case of chloro- and bromoacetic acids, and B3PW91/3-21G in the case of iodoacetic acid. The results obtained are: $C^{o}_{p,\mathrm{m}}(\mathrm{C_2H_3O_2Cl,\ g}) = 78.3\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $C^{o}_{p,\mathrm{m}}(\mathrm{C_2H_3O_2Br,\ g}) = 79.9\ \mathrm{J\,K^{-1}\,mol^{-1}}$, and $C^{o}_{p,\mathrm{m}}(\mathrm{C_2H_3O_2I,\ g}) = 81.0\ \mathrm{J\,K^{-1}\,mol^{-1}}$. The heat capacities of chloro- and bromoacetic acids were also calculated at the B3PW91/3-21G level leading to $79.1\ \mathrm{J\,K^{-1}\,mol^{-1}}$ and $79.7\ \mathrm{J\,K^{-1}\,mol^{-1}}$, respectively. These results are very similar to those obtained at the higher B3LYP/6-311 + G(d,p) level suggesting that the value of the gas phase heat capacity of iodoacetic acid indicated above should also be reliable.

The heat capacity of crystalline chloroacetic acid, at 298.15 K, proposed in this work ($106.7 \pm 2.0\ \mathrm{J\,K^{-1}\,mol^{-1}}$), is considerably different from the average value of $144\ \mathrm{J\,K^{-1}\,mol^{-1}}$, in the range 288–318 K, reported by Pickering.[5, 7, 8] Note, however, that accuracy of this result was classified as poor in the critical compilation by Domalski and Hearing.[8] A large discrepancy is also observed between the gas phase heat capacity of chloroacetic acid at 298.15 K, obtained in this work ($78.3\ \mathrm{J\,K^{-1}\,mol^{-1}}$) and the corresponding value of $136.02\ \mathrm{J\,K^{-1}\,mol^{-1}}$ recommended in the literature.[9] This latter value, which was also judged to have low accuracy by Frenkel et al.,[9] seems too high, since it is greater than the experimental heat capacity of chloroacetic acid in the crystalline state indicated above.

The enthalpies of fusion of the acids were also measured by DSC as $\Delta_{\mathrm{fus}}H^{o}_{\mathrm{m}}(\mathrm{C_2H_3O_2Cl}) = (16.3 \pm 0.4)\ \mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{fus}}H^{o}_{\mathrm{m}}(\mathrm{C_2H_3O_2Br}) = (13.9 \pm 0.3)\ \mathrm{kJ\,mol^{-1}}$, and $\Delta_{\mathrm{fus}}H^{o}_{\mathrm{m}}(\mathrm{C_2H_3O_2I}) = (15.5 \pm 0.7)\ \mathrm{kJ\,mol^{-1}}$. The obtained values correspond to the temperatures of fusion $T_{\mathrm{fus}} = (334.8 \pm 0.3)$ K, $T_{\mathrm{fus}} = (319.2 \pm 0.7)$ K, and $T_{\mathrm{fus}} = (355.1 \pm 0.1)$ K, respectively, measured at the onset of each DSC peak. The uncertainties quoted for $\Delta_{\mathrm{fus}}H^{o}_{\mathrm{m}}$ and $T_{\mathrm{fus}}$ represent twice the standard deviation of the mean of six independent determinations in the case of chloroacetic acid and four determinations in the case of bromo- and iodoacetic acids. The enthalpy of fusion of chloroacetic acid obtained in this work is significantly different from the value $\Delta_{\mathrm{fus}}H^{o}_{\mathrm{m}}(\mathrm{C_2H_3O_2Cl}) = 12.3\ \mathrm{kJ\,mol^{-1}}$, reported in the literature at $T_{\mathrm{fus}} = 334.4$ K.[10]

To our knowledge, no heat capacity and enthalpy of fusion data have been published for bromo- and iodoacetic acids previously to this work.

**Knudsen effusion measurements**: The vapor pressures, $p$, of chloro-, bromo-, and iodoacetic acids (given as Supporting Information) were obtained by Knudsen effusion experiments. The values of $p$ were calculated from Equations (1) and (2),[11] where $m$ is the mass loss during the time $t$, $A = 3.991 \times 10^{-3}\ \mathrm{cm^2}$, $l = 2.09 \times 10^{-3}$ cm, and $r = 3.564 \times 10^{-2}$ cm are the area, the thickness, and the radius of the effusion hole,

$$p = \frac{m}{At}\left(\frac{2\pi RT}{M}\right)^{1/2}\left(\frac{8r+3l}{8r}\right)\left(\frac{2\lambda}{2\lambda+0.48r}\right) \tag{1}$$

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 p} \tag{2}$$

$M$ is the molar mass of the compound, $R$ is the gas constant, $T$ is the absolute temperature and $\lambda$ is the mean free path given by Equation (2).[12] Here $k$ represents the Boltzmann constant and $\sigma$ the collision diameter. The collision diameters of chloro- and bromoacetic acids were estimated as $5.28 \times 10^{-8}$ cm and $5.39 \times 10^{-8}$ cm, respectively, from projections of the corresponding molecular structures[13] in the $x$, $y$, and $z$ planes. The van der Waals radii of the carbon, hydrogen, and halogen atoms were taken into account in the calculation.[14] A collision diameter of $5.50 \times 10^{-8}$ cm was calculated by the same procedure for iodoacetic acid with a hypothetical structure obtained by replacing Cl by I in the chloroacetic acid structure. Since the mean free path in Equation (2) is pressure dependent, an iterative method was used to obtain the vapor pressure of the compounds by Equations (1) and (2). As a first approximation, $p$ was calculated by ignoring the $\lambda$ dependent term in Equation (1). The result obtained was subsequently used to derive $\lambda$ from Equation (2). The calculated mean free path was introduced in Equation (1) and a second $p$ value was calculated. The iteration was continued until the difference between successive values of $p$ was smaller than $10^{-8}$ Pa.

The vapor pressure data were fitted to Equation (3):[15]

$$\ln p = a + \frac{b}{T} \tag{3}$$

leading to the results in Table 1. The enthalpies of sublimation of chloro-, bromo-, and iodoacetic acids at $T_{\mathrm{m}}$ (the average of the highest and lowest temperatures of the range covered in each series of experiments) are given by $\Delta_{\mathrm{sub}}H^{o}_{\mathrm{m}} = -Rb$. The corresponding values at 298.15 K were derived from Equation (4):

$$\Delta_{\mathrm{sub}}H^{o}_{\mathrm{m}}(298.15\ \mathrm{K}) = \Delta_{\mathrm{sub}}H^{o}_{\mathrm{m}}(T_{\mathrm{m}}) + \Delta_{\mathrm{sub}}C^{o}_{p,\mathrm{m}}(298.15\ \mathrm{K} - T_{\mathrm{m}}) \tag{4}$$

Table 1. Values of the constants in Equation (3) and enthalpies of sublimation of chloro-, bromo-, and iodoacetic acids.

| Compound | $T_m$/K | $a$ | $-b$ | $\Delta_{sub}H^{o}_{m}(T_m)$/kJ mol$^{-1}$ | $\Delta_{sub}H^{o}_{m}$(298.15 K)/kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| $C_2H_3O_2Cl$ | 281.95 | 35.494 ± 0.392 | 9940.54 ± 110.15 | 82.65 ± 0.92 | 82.19 ± 0.92 |
| $C_2H_3O_2Br$ | 280.32 | 35.773 ± 1.268 | 10102.07 ± 354.99 | 83.99 ± 2.95 | 83.50 ± 2.95 |
| $C_2H_3O_2I$ | 279.13 | 35.106 ± 0.438 | 10488.02 ± 122.68 | 87.20 ± 1.02 | 86.47 ± 1.02 |

where the $\Delta_{sub}C^{o}_{p,m} = C^{o}_{p,m}(g) - C^{o}_{p,m}(cr)$ data were calculated from the heat capacities of the gaseous and solid compounds at 298.15 K, referred to above. The uncertainties quoted for $a$, $b$, and $\Delta_{sub}H^{o}_{m}$ include Student's factor for 95% confidence level ($t = 2.365$ for chloro- and bromoacetic acids and $t = 2.447$ for iodoacetic acid).[16]

**Combustion calorimetry**: Detailed results of the combustion calorimetric experiments are given as Supporting Information and led to the standard molar energies ($\Delta_C U^{o}_{m}$) and enthalpies of combustion ($\Delta_C H^{o}_{m}$) of the acids, at 298.15 K (Table 2). These values refer to the reactions:

$$C_2H_3O_2Cl\,(cr) + \tfrac{3}{2}O_2\,(g) + 599\,H_2O\,(l) \rightarrow 2\,CO_2\,(g) + HCl\cdot 600\,H_2O\,(l) \quad (5)$$

$$C_2H_3O_2Br\,(cr) + \tfrac{3}{2}O_2\,(g) + 599\,H_2O\,(l) \rightarrow 2\,CO_2\,(g) + HBr\cdot 600\,H_2O\,(l) \quad (6)$$

$$C_2H_3O_2I\,(cr) + \tfrac{7}{4}O_2\,(g) \rightarrow 2\,CO_2\,(g) + \tfrac{3}{2}H_2O\,(l) + \tfrac{1}{2}I_2\,(cr) \quad (7)$$

where the uncertainties quoted represent twice the over-all standard deviation of the mean and include the contributions from the calibration with benzoic acid and from the energy of combustion of the auxiliary oil.[17] From the $\Delta_C H^{o}_{m}$ values indicated above and $\Delta_f H^{o}_{m}(CO_2,\ g) = -(393.51 \pm 0.13)$ kJ mol$^{-1}$,[18] $\Delta_f H^{o}_{m}(H_2O,\ l) = -(285.830 \pm 0.040)$ kJ mol$^{-1}$,[18] $\Delta_f H^{o}_{m}(HCl\cdot 600\,H_2O,\ l) = -166.619$ kJ mol$^{-1}$,[19] and $\Delta_f H^{o}_{m}(HBr\cdot 600\,H_2O,\ l) = -120.924$ kJ mol$^{-1}$,[19] it was possible to derive the standard molar enthalpies of formation of the acids in the crystalline state indicated in Table 2. Also included in this table are the corresponding enthalpies of formation in the gaseous state, which were calculated from the $\Delta_f H^{o}_{m}$(cr) values and the enthalpies of sublimation in Table 1. As mentioned in the Introduction, only the enthalpy of formation of chloroacetic acid in the crystalline state had been previously measured by Smith et al.[3] The value reported by these authors, $\Delta_f H^{o}_{m}(C_2H_3O_2Cl,\ cr) = -(510.5 \pm 8.3)$ kJ mol$^{-1}$,[3, 20] despite its large uncertainty interval, is in good agreement with $\Delta_f H^{o}_{m}(C_2H_3O_2Cl,\ cr) = -(509.74 \pm 0.49)$ kJ mol$^{-1}$ obtained in this work.

Table 2. Standard molar energies and enthalpies of combustion, and enthalpies of formation of chloro-, bromo-, and iodoacetic acids, at 298.15 K. Data in kJ mol$^{-1}$.

| Compound | $-\Delta_C U^{o}_{m}$ | $-\Delta_C H^{o}_{m}$ | $-\Delta_f H^{o}_{m}$(cr) | $-\Delta_f H^{o}_{m}$(g) |
|---|---|---|---|---|
| $C_2H_3O_2Cl$ | 728.49 ± 0.41 | 729.73 ± 0.41 | 509.74 ± 0.49 | 427.55 ± 1.04 |
| $C_2H_3O_2Br$ | 728.03 ± 1.05 | 726.79 ± 1.05 | 466.98 ± 1.08 | 383.48 ± 3.14 |
| $C_2H_3O_2I$ | 796.61 ± 1.51 | 800.33 ± 1.51 | 415.44 ± 1.53 | 328.97 ± 1.84 |

**DFT calculations**: The standard enthalpy of formation of the $CH_2COOH$ radical was estimated according to the following procedure. First, the enthalpy of the isodesmic and isogyric reaction (8) ($\Delta_r H^{o}_{m}$) was computed for X = H, Cl, Br, and I (Table 3). Second, Equation (9) was used to derive

$$XCH_2COOH(g) + C_2H_5(g) \rightarrow CH_2COOH(g) + C_2H_5X(g) \quad (8)$$

$$\begin{aligned}\Delta_f H^{o}_{m}(CH_2COOH,\ g) = {} & \Delta_r H^{o}_{m} - \Delta_f H^{o}_{m}(C_2H_5X,\ g) + \Delta_f H^{o}_{m}(C_2H_5,\ g) \\ & + \Delta_f H^{o}_{m}(XCH_2COOH,\ g)\end{aligned} \quad (9)$$

$\Delta_f H^{o}_{m}(CH_2COOH,\ g)$ from *each* theoretical result for that reaction enthalpy, by using the enthalpy of formation data for the gaseous haloacetic acids in Table 2 and $\Delta_f H^{o}_{m}(CH_3COOH,\ g) = -432.8 \pm 2.5$ kJ mol$^{-1}$,[20] $\Delta_f H^{o}_{m}(C_2H_6,\ g) = -83.8 \pm 0.3$ kJ mol$^{-1}$,[20] $\Delta_f H^{o}_{m}(C_2H_5,\ g) = 119 \pm 2$ kJ mol$^{-1}$,[21] $\Delta_f H^{o}_{m}(C_2H_5Cl,\ g) = -112.1 \pm 1.1$ kJ mol$^{-1}$,[20] $\Delta_f H^{o}_{m}(C_2H_5Br,\ g) = -61.9 \pm 1.6$ kJ mol$^{-1}$,[20] and $\Delta_f H^{o}_{m}(C_2H_5I,\ g) = -8.1 \pm 2.2$ kJ mol$^{-1}$.[20] The results are collected in Table 4.

Table 3. Theoretically calculated enthalpies of reaction (8) at 298.15 K.

| Method | $-\Delta_r H^{o}_{m}$/kJ mol$^{-1}$ | | | |
|---|---|---|---|---|
| | X = H | X = Cl | X = Br | X = I |
| B3PW91/3-21G | 3.6 | 44.6 | 36.5 | 31.3 |
| B3PW91/6-31G(d,p) | 11.8 | 38.7 | 36.1 | |
| B3PW91/6-311 + G(d,p) | 8.2 | 38.2 | 35.9 | |
| B3LYP/6-311 + G(d,p) | 9.8 | 40.3 | 37.2 | |

Table 4. Calculated values for the standard enthalpy of formation of $CH_2COOH$ at 298.15 K.

| Method | $-\Delta_f H^{o}_{m}(CH_2COOH,\ g)$/kJ mol$^{-1}$ | | | |
|---|---|---|---|---|
| | X = H | X = Cl | X = Br | X = I |
| B3PW91/3-21G | 233.6 | 241.1 | 239.1 | 233.2 |
| B3PW91/6-31G(d,p) | 241.8 | 235.2 | 238.7 | |
| B3PW91/6-311 + G(d,p) | 238.2 | 234.7 | 238.5 | |
| B3LYP/6-311 + G(d,p) | 239.8 | 236.8 | 239.8 | |

It is noted in Table 3 that the B3PW91 and the B3LYP functionals lead to similar $\Delta_r H^{o}_{m}$ values for each X, particularly when the two larger basis sets were used. On the other hand, Table 4 shows that the values of $\Delta_f H^{o}_{m}(CH_2COOH,\ g)$ obtained from the several $\Delta_r H^{o}_{m}$ results (Table 3) and the corresponding experimental enthalpy of formation data are in excellent agreement. This supports the reliability of the DFT results and indicates a very good thermodynamic consistency between the theoretical reaction enthalpies and the experimental standard enthalpy of formation data. The selected value for $\Delta_f H^{o}_{m}(CH_2COOH,\ g)$ of $-(238.0 \pm 2.0)$ kJ mol$^{-1}$ is a weighed average of the results in Table 4. It is in excellent agreement with early ab initio results by Yu et al.,[22] $-(239.5 \pm 9.3)$ kJ mol$^{-1}$ and $-243.8$ kJ mol$^{-1}$, and by Leroy et al.[23], $-238.7$ kJ mol$^{-1}$. It is also in good agreement with a result obtained from flowing afterglow experiments by Wenthold and Squires,[24] $-(248.9 \pm 12.1)$ kJ mol$^{-1}$ and with an estimate by Orlov et al.,[25] −243.1 kJ mol$^{-1}$. However, our calculated result for $\Delta_f H^\circ_m$(CH$_2$COOH, g) disagrees with an electron-impact value obtained by Holmes et al.,[26] −(257.7 ± 12.6) kJ mol$^{-1}$.

**X−CH$_2$COOH bond dissociation enthalpies**: Our selection for $\Delta_f H^\circ_m$(CH$_2$COOH, g), −(238.0 ± 2.0) kJ mol$^{-1}$, together with the enthalpies of formation of H (217.998 ± 0.006 kJ mol$^{-1}$),[18] Cl (121.301 ± 0.008 kJ mol$^{-1}$),[18] Br (111.87 ± 0.12 kJ mol$^{-1}$),[18] I (106.76 ± 0.04 kJ mol$^{-1}$),[18] and $\Delta_f H^\circ_m$(XCH$_2$COOH, g) (X = H, Cl, Br, I), yield the following C−X bond dissociation enthalpies at 298.15 K: $DH^\circ$(H−CH$_2$COOH) = (412.8 ± 3.2) kJ mol$^{-1}$, $DH^\circ$(Cl−CH$_2$COOH) = (310.9 ± 2.2) kJ mol$^{-1}$, $DH^\circ$(Br−CH$_2$COOH) = (257.4 ± 3.7) kJ mol$^{-1}$, and $DH^\circ$(I−CH$_2$COOH) = (197.8 ± 2.7) kJ mol$^{-1}$. These values are compared in Table 5 with the corresponding C−X bond dissociation enthalpies in XCH$_3$, XC$_2$H$_5$, XC$_2$H$_3$, and XC$_6$H$_5$, which were calculated from literature data.[18, 20, 21, 27, 28]

Table 5. R−X bond dissociation enthalpies in kJ mol$^{-1}$. Pauling electronegativities[a] of the R and X fragments are given in parentheses.

| | X | | | | |
|---|---|---|---|---|---|
| R | H (2.25) | Cl (3.10) | Br (2.95) | I (2.74) | R |
| CH$_2$COOH (2.74) | 412.8 ± 3.2 | 310.9 ± 2.2 | 257.4 ± 3.7 | 197.8 ± 2.7 | 342.7 ± 4.3 |
| CH$_3$ (2.31) | 438.8 ± 0.6 | 349.6 ± 0.6 | 293.7 ± 1.4 | 238.8 ± 1.5 | 376.6 ± 0.6 |
| C$_2$H$_5$ (2.32) | 420.8 ± 2.0 | 352.4 ± 2.3 | 292.8 ± 2.6 | 233.9 ± 3.0 | 363.7 ± 2.9 |
| C$_2$H$_3$ (2.43) | 465.1 ± 3.3 | 383.7 ± 3.5 | 332.3 ± 3.8 | | 489.2 ± 4.8 |
| C$_6$H$_5$ (2.49) | 465.5 ± 3.5 | 399.4 ± 1.7 | 336.6 ± 4.4 | 272.0 ± 6.8 | 478.8 ± 5.1 |

[a] From ref. [35, 36].

Plots of $DH^\circ$(R−X) versus $DH^\circ$(H−X) (X = Cl, Br, I; R = CH$_3$, C$_2$H$_5$, C$_2$H$_3$, C$_6$H$_5$, and CH$_2$COOH), obtained from the $DH^\circ$(R−X) data in Table 5 and $DH^\circ$(H−Cl) = (432.61 ± 0.10) kJ mol$^{-1}$, $DH^\circ$(H−Br) = (366.16 ± 0.20) kJ mol$^{-1}$, and $DH^\circ$(H−I) = (298.11 ± 0.11) kJ mol$^{-1}$, calculated from literature data,[18] are shown in Figure 1. The various lines have similar slopes (0.84 for R = CH$_2$COOH, 0.83 for R = CH$_3$, 0.88 for R = C$_2$H$_5$, 0.77 for R = C$_2$H$_3$, and 0.95 for R = C$_6$H$_5$) and correlation coefficients higher than 0.999. This type of representations have been used by us[29] and others[30–32] to estimate thermochemical data and to evidence interesting aspects of the bonding energetics in a variety of organic, inorganic, and organometallic molecules. Three subsets of lines can be distinguished in Figure 1: a) R = C$_2$H$_3$ and C$_6$H$_5$; b) R = CH$_3$ and C$_2$H$_5$; and c) R = CH$_2$COOH. The decrease of $DH^\circ$(R−X) from subset a) to b) 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$_2$H$_3$ and X−C$_6$H$_5$ bonds have a higher s character than the sp$^3$ carbons involved in the X−CH$_3$ and X−C$_2$H$_5$ bonds, and it is well-known that the C−X bond dissociation enthalpies increase with increasing carbon s character.[33] The additional decrease of $DH^\circ$(X−R) from subsets b) to c) may be due to the fact that the formation of the carboxymethyl radical upon breaking of the C−X bond involves a larger relaxation energy than the formation of the methyl or ethyl radicals. Similar arguments can be used to explain the trends observed in Table 5 for $DH^\circ$(R−H).

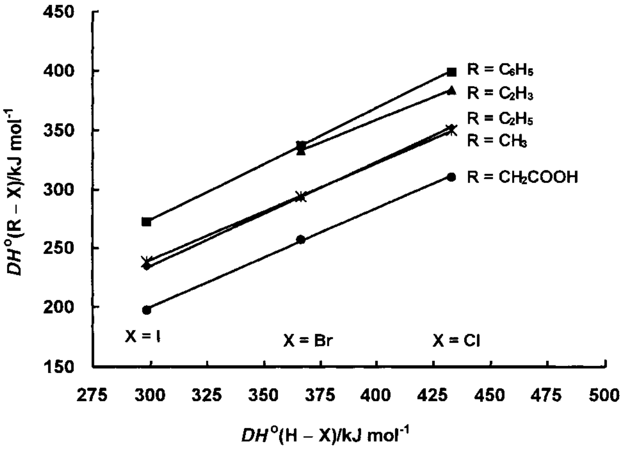

Figure 1. R−X bond dissociation enthalpies (from Table 5) versus the corresponding H−X bond dissociation enthalpies for X = Cl, Br, I and R = CH$_3$, C$_2$H$_5$, C$_2$H$_3$, C$_6$H$_5$, and CH$_2$COOH.

Interestingly the major qualitative trends exhibited by the carbon halogen bond dissociation enthalpies in Table 5 and Figure 1 can also be predicted based on Pauling's electrostatic–covalent model.[34] Applying Pauling's arithmetic mean expression to both R−X and H−X yields:

$$DH^\circ(\text{R–X}) = \frac{DH^\circ(\text{R}-\text{R}) + DH^\circ(\text{X}-\text{X})}{2} + 96.232\,(\chi_\text{R} - \chi_\text{X})^2 \tag{10}$$

$$DH^\circ(\text{H–X}) = \frac{DH^\circ(\text{H}-\text{H}) + DH^\circ(\text{X}-\text{X})}{2} + 96.232\,(\chi_\text{H} - \chi_\text{X})^2 \tag{11}$$

where $\chi_\text{H}$, $\chi_\text{X}$, and $\chi_\text{R}$ are the electronegativities of H, X, and R, respectively. Subtraction of Equation (11) from Equation (10) leads to:

$$\begin{aligned} DH^\circ(\text{R–X}) = DH^\circ(\text{H–X}) &+ \frac{DH^\circ(\text{R}-\text{R}) - DH^\circ(\text{H}-\text{H})}{2} \\ &+ 96.232\,[(\chi_\text{R} - \chi_\text{X})^2 - (\chi_\text{H} - \chi_\text{X})^2] \end{aligned} \tag{12}$$

As shown in Figure 2, there is a good linear correlation between the experimental $DH^\circ$(R−X) values in Table 5 and the corresponding $DH^\circ$(R−X)$_\text{calcd}$ values calculated from Equation (12), by using $DH^\circ$(H−H) = 435.996 ± 0.008 kJ mol$^{-1}$, $DH^\circ$(H − X), and the $DH^\circ$(R − R) and elec-

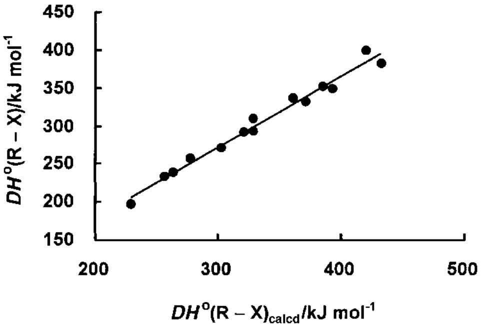

Figure 2. Experimental R−X bond dissociation enthalpies (from Table 5), $DH^\circ$(R−X), versus the corresponding values calculated from Equation (12), $DH^\circ$(R−X)$_\text{calcd}$, for X = Cl, Br, I, and R = CH$_3$, C$_2$H$_5$, C$_2$H$_3$, C$_6$H$_5$, and CH$_2$COOH.

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tronegativity[35, 36] data given in Table 5, respectively. The line in Figure 2 corresponds to Equation (13):

$$DH^\circ(\mathrm{R{-}X}) = (0.926 \pm 0.037)\ DH^\circ(\mathrm{R{-}X})_{\mathrm{calcd}} - (5.14 \pm 12.61) \qquad (13)$$

with a regression coefficient of 0.99. The average error in the estimation of $DH^\circ(\mathrm{R{-}X})$ from Equation (13) is 6.4 kJ mol$^{-1}$.

It is finally noted that the differences $DH^\circ(\mathrm{X{-}CH_3}) - DH^\circ(\mathrm{X{-}CH_2COOH})$ and $DH^\circ(\mathrm{X{-}C_2H_5}) - DH^\circ(\mathrm{X{-}CH_2COOH})$ in Table 5 are smaller for X = H than for X = halogen. This is consistent with the predicted variation in the ionic character of the R–X bonds based on the differences in the electronegativities of the R and X fragments. According to Pauling's covalent–electrostatic model, bonds are strengthened by an increase of their ionic character. While the ionic character of the H–CH$_2$COOH bond is much larger than the ionic character of the H–CH$_3$ and H–C$_2$H$_5$ bonds ($|\chi_{\mathrm{H}} - \chi_{\mathrm{CH_2COOH}}| = 0.49$, $|\chi_{\mathrm{H}} - \chi_{\mathrm{CH_3}}| = 0.06$, $|\chi_{\mathrm{H}} - \chi_{\mathrm{C_2H_5}}| = 0.07$), the opposite is observed for the X–CH$_2$COOH, X–CH$_3$, and X–C$_2$H$_5$ bonds when X = Cl, Br, or I ($|\chi_{\mathrm{Cl}} - \chi_{\mathrm{CH_2COOH}}| = 0.36$, $|\chi_{\mathrm{Cl}} - \chi_{\mathrm{CH_3}}| = 0.79$, $|\chi_{\mathrm{Cl}} - \chi_{\mathrm{C_2H_5}}| = 0.78$; $|\chi_{\mathrm{Br}} - \chi_{\mathrm{CH_2COOH}}| = 0.21$, $|\chi_{\mathrm{Br}} - \chi_{\mathrm{CH_3}}| = 0.64$, $|\chi_{\mathrm{Br}} - \chi_{\mathrm{C_2H_5}}| = 0.63$; $|\chi_{\mathrm{I}} - \chi_{\mathrm{CH_2COOH}}| = 0.00$, $|\chi_{\mathrm{I}} - \chi_{\mathrm{CH_3}}| = 0.43$, $|\chi_{\mathrm{I}} - \chi_{\mathrm{C_2H_5}}| = 0.42$).

## Experimental Section

**General**: $^1$H NMR spectra were obtained on a Varian Gemini (200 MHz) instrument for chloroacetic acid and a Bruker AMX (400 MHz) for bromo- and iodoacetic acid, using CDCl$_3$ solutions at ambient temperature. Chemical shifts relative to TMS were calculated using CHCl$_3$ as an internal standard. IR spectra were recorded on a Perkin–Elmer PE 1720 using KBr pellets. X-ray powder diffractrograms were recorded in a Philips PW1050/25 diffractometer with a nickel-filtered Cu$_{\mathrm{K}\alpha}$ radiation ($\lambda = 1.54178$ Å) equipped with a proportional counter. Melting temperatures and enthalpies of melting where determined in a Setaram DSC 121 Differential Scanning Calorimeter at a scan rate of 2 K min$^{-1}$. The samples were sealed inside aluminium crucibles and argon was used as the purging gas.

**Materials**

***α*-Chloroacetic acid**: Chloroacetic acid (Merck, p.a.) was recrystallized from diethyl ether and sublimed at a temperature of 298 K and a pressure of 10 Pa. The obtained sample ($\alpha$ phase) was kept in a Schlenk tube under argon prior to combustion. The phase identification and phase purity were checked by X-ray powder diffraction (main reflections: 18.5, 23.9, 25.7, 27.9, 37.5, 39.0, 47.4°, 2$\theta$).[13a] $T_{\mathrm{fus}} = (334.8 \pm 0.3)$ K (average of six measurements); IR (KBr): $\tilde{\nu} = 3008$, 2959 (C–H), 1733 (C=O), 1418, 1407, 1394 cm$^{-1}$ (O–H); elemental analysis calcd (%) for C$_2$H$_3$O$_2$Cl: C 25.4, H 3.0; found C 25.1, H 3.0 (average of two measurements); $^1$H NMR (200 MHz, CDCl$_3$): $\delta = 4.12$ (s, 2-H), 11.84 (s, 1-H).

**Bromoacetic acid (form I)**: Bromoacetic acid (Merck, p.a.) was recrystallized from diethyl ether and sublimed at a temperature of 292 K and a pressure of 10 Pa. The obtained sample (form I) was kept in a Schlenk tube under argon prior to combustion. The phase identification and phase purity were checked by X-ray powder diffraction (main reflections: 7.4, 22.4, 23.5, 25.3, 26.0, 27.1, 30.0, 31.1, 35.5, 37.8, 43.2°, 2$\theta$).[13b] $T_{\mathrm{fus}} = (319.2 \pm 0.7)$ K (average of four measurements); IR (KBr): $\tilde{\nu} = 3035$, 2962 (C–H), 1726 (C=O), 1403 cm$^{-1}$ (O–H); elemental analysis calcd (%) for C$_2$H$_3$O$_2$Br: C 17.3, H 2.1; found C 17.2, H 2.3 (average of three measurements); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 4.15$ (s, 2-H).

**Iodoacetic acid**: Iodoacetic acid (Merck, p.a.) was recrystallized from diethyl ether and sublimed at a temperature of 291 K and a pressure of 10 Pa. The obtained sample was kept in a Schlenk tube under argon prior to combustion. The main reflections found in the X-ray powder diffractogram are: 7.5, 21.7, 22.5, 23.7, 25.8, 27.2, 30.1, 38.0, 42.4°, 2$\theta$. $T_{\mathrm{fus}} = (355.1 \pm 0.1)$ K (average of four measurements); IR (KBr): $\tilde{\nu} = 3051$ (C–H), 1686 (C=O), 1427, 1391 cm$^{-1}$ (O–H); elemental analysis calcd (%) for C$_2$H$_3$O$_2$I: C 25.4, H 3.0; found C 25.1, H 3.0 (average of two measurements); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.72$ (s, 2-H).

**Heat capacity and enthalpy of fusion measurements**: The temperatures and enthalpies of fusion, and the solid state heat capacities of chloro-, bromo-, and iodoacetic acids were measured with a Setaram DSC 121 differential scanning calorimeter. The mass of sample used was about 10 mg in the enthalpy of fusion and about 90–110 mg in heat capacity measurements. In all experiments the samples were sealed in aluminium crucibles and studied at a scan rate of 2 K min$^{-1}$, using argon as the purging gas. The experimental method and the data handling procedure used in the heat capacity determinations were previously described.[37] The temperature and heat flux scales of the calorimeter were calibrated by determining the temperatures and enthalpies of fusion of the following standard substances: benzoic acid (B.D.H. thermochemical standard), indium (Perkin–Elmer, 99.999%), tin (Goodfellow, SN006110, 99.995%), lead (Goodfellow, PB006100, 99.999%), and zinc (Perkin–Elmer, 99.999%).

**Knudsen effusion measurements**: The enthalpies of sublimation of chloro-, bromo-, and iodoacetic acids were determined with the Knudsen effusion apparatus and operating procedure previously described.[38] The temperature of the water bath was controlled to ±0.01 K with a Haake ED Unitherm thermostat using a Haake EK12 cryostat as the heat sink. The temperature of the Knudsen cell was measured with a Tecnisis 100 Ω platinum resistance thermometer (Pt 100) calibrated against a Hewlett–Packard (HP2804A) quartz thermometer. The Pt 100 sensor was embedded in the bronze block containing the Knudsen cell and was connected in a four wire configuration to a Keithley 2000 multimeter. The average of all temperature readings acquired in a constant 10 s interval was stored in the buffer memory of the multimeter. The mean value of the total number of readings accumulated in the buffer during a run was used as the temperature of the experiment. The mass loss from the sample was determined by weighing the cell to $\pm 10^{-5}$ g with a Mettler AT 201 balance.

**Combustion calorimetry**: The isoperibol rotating-bomb combustion calorimeter used in this work has been described previously.[39] The bomb with a volume of 0.258 dm$^3$ was of stainless steel lined with platinum; all the internal fittings were made from platinum. The sample container was a platinum crucible supported by a platinum ring inside the bomb. The total mass of the crucible and the ring was about 11.7 g. In a typical experiment, a pellet of the sample and the *n*-hexadecane (Aldrich, Gold Label) used as combustion aid, were weighted inside the crucible in a Mettler AE 240 balance with a precision of $\pm 10^{-5}$ 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$_{0.843}$ was weighted with a precision of $\pm 10^{-5}$ g and tied to the platinum wire. The crucible was adjusted to the bomb head and the cotton thread fuse was placed in contact with the sample, without touching the crucible walls. In the case of chloro- and bromoacetic acids, 20 cm$^3$ and 25 cm$^3$, respectively, of a 0.09016 mol dm$^{-3}$ As$_2$O$_3$ 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.[4a,d, 40, 41] Since mixtures of X$_2$ and HX of variable composition are always formed in the combustion of chlorine or bromine organic compounds this method enabled to simplify the analysis of the final state.[4a] In the experiments with iodoacetic acid the bomb contained 10 cm$^3$ of a 0.909 mol dm$^{-3}$ KI aqueous solution to achieve a quantitative conversion of the I$_2$ formed in the combustion to I$_3^-$(aq).[42] Although only elemental iodine is found in the combustion products of organoiodine compounds,[4a] 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.[42] After the introduction of the bomb solution, 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 bomb was then charged with oxygen at a pressure of 3.04 MPa and 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 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 of the fore, main, and after periods was about 20 minutes 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.[43] The $HNO_3$ formed from traces of atmospheric $N_2$ remaining inside the bomb was analyzed by the Devarda's alloy method.[44] The extent of the reactions of the elemental halogens formed in the combustions with the arsenious oxide or potassium iodate solutions were found by titrating the final bomb solutions with sodium thiosulphate (0.100 mol dm$^{-3}$).[44] A small residue of carbon was found in the crucible at the end of some of the experiments. The mass of this residue was determined as follows. The crucible containing the residue was dried for about 5 min with a hair dryer, cooled to room temperature inside a desiccator, and weighed. After heating it with a Bunsen burner flame to eliminate the residue, the crucible was transferred to the desiccator, and weighed a second time. The mass of residue formed in the experiment was taken as the mass difference between the first and second weighings.

**DFT calculations**: The calculations reported in this study have been carried out with the Gaussian-94/DFT program.[45] The geometries have been fully optimized and the total energies were calculated using the Becke's three-parameter hybrid method[46] with the Perdew and Wang PW91[47] correlation functional (B3PW91) and the Lee, Yang, and Parr LYP[48] correlation functional (B3LYP). The basis set were the 3-21G[49], 6-31G(d,p),[50] and 6-311 + G(d,p).[51] Total energies ($E$) were calculated from Equation (14):

$$E = V_{NN} + H^{core} + V_{ee} + E_X[\rho] - E_C[\rho] \qquad (14)$$

where $V_{NN}$ is the nuclear-nuclear interaction, $H^{core}$ is a mono-electronic contribution to the total energy, including electron kinetic and electron–nuclear interaction energies, and $V_{ee}$ is the coulombic interaction between the electrons. $E_X[\rho]$ and $E_C[\rho]$ are the exchange and correlation energies, functionals of the electronic density $\rho$. All the total energies, given as Supporting Information, were corrected with the zero-point vibrational energies calculated at the same theoretical level.

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[1] J. March, *Advanced Organic Chemistry*, 4th ed., Wiley, New York, **1992**, p. 412.

[2] *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed. (Eds.: W. Gerhartz, Y. S. Yamamoto, F. T. Campbell, R. Pfefferkorn, J. F. Rounsaville), VCH, Weinheim, **1986**.

[3] L. Smith, L. Bjellerup, S. Krook, H. Westermark, *Acta Chem. Scand.* **1953**, *7*, 65–86.

[4] a) L. Smith, W. N. Hubbard in *Experimental Thermochemistry*, *Vol. 1* (Ed.: F. D. Rossini), Wiley, New York, **1956**, Chapter 8; b) A. J. Head, W. D. Good in *Experimental Chemical Thermodynamics*, *Vol. 1* (Eds.: S. Sunner, M. Månsson), Pergamon Press, London, **1979**, Chapter 9; c) S. N. Hajiev in *Thermochemistry and Equilibria of Organic Compounds* (Ed.: M. Frenkel), VCH, New York, **1993**, Book I, Chapter 4; d) M. E. Minas da Piedade in *Energetics of Stable Molecules and Reactive Intermediates*, *Vol. 535* (Ed.: M. E. Minas da Piedade), NATO Science Series C, Kluwer, Dordrecht, **1999**, Chapter 2.

[5] *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69 (Eds.: W. G. Mallard, P. J. Linstrom), National Institute of Standards and Technology, Gaithersburg, November **1998** (http://webbook.nist.gov/chemistry).

[6] a) A. E. Martell, R. M. Smith, *Critical Stability Constants*, *Vol. 3*, Plenum Press, New York, **1977**; b) K. Izutsu, *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents*, IUPAC Chemical Data Series No. 35, Blackwell, Oxford, **1990**.

[7] S. U. Pickering, *J. Chem. Soc.* **1895**, *67*, 664–684.

[8] E. S. Domalski, E. D. Hearing, *J. Phys. Chem. Ref. Data* **1996**, *25*, 1–525.

[9] M. Frenkel, K. N. Marsh, R. C. Wilhoit, G. J. Kabo, G. N. Roganov, *Thermodynamics of Organic Compounds in the Gas State*, *Vol. I*, Thermodynamics Research Center, College Station, **1994**.

[10] W. E. Acree, Jr., *Thermochim. Acta* **1991**, *189*, 37–56.

[11] a) J. W. Edwards, G. L. Kington, *Trans. Faraday Soc.* **1962**, *58*, 1323–1333; b) J. T. S. Andrews, E. F. Westrum, Jr., N. Bjerrum, *J. Organometal. Chem.* **1969**, *17*, 293–302.

[12] P. W. Atkins, *Physical Chemistry*, 4th ed., Oxford University Press, Oxford, **1993**, p. 732.

[13] a) J. A. Kanters, G. Roelofsen, *Acta Crystallogr.* **1976**, *B32*, 3328–3331; b) L. Leiserowitz, D. vor der Brück, *Crystallogr. Struct. Commun.* **1975**, *4*, 647–651.

[14] J. E. Huheey, *Inorganic Chemistry*: *Principles of Structure and Reactivity*, 2nd ed., Harper&Row, London, **1978**, p. 184.

[15] J. D. Cox, G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, **1970**.

[16] G. A. Korn, T. M. Korn, *Mathematical Handbook for Scientists and Engineers*, McGraw-Hill, New York, **1968**.

[17] a) G. Olofsson in *Experimental Chemical Thermodynamics*, *Vol. 1* (Eds.: S. Sunner, M. Månsson), Pergamon Press, London, **1979**, Chapter 6; b) L. Bjellerup, *Acta Chem. Scand.* **1961**, *15*, 121–140.

[18] *CODATA Key Values for Thermodynamics* (Eds.: J. D. Cox, D. D. Wagman, V. A. Medvedev), Hemisphere, New York, **1989**.

[19] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall, *The NBS Tables of Chemical Thermodynamics Properties*, *J. Phys Chem. Ref. Data* **1982**, *11*, Supplement no. 2.

[20] J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds*, *Vol. I*, Thermodynamics Research Center Data Series, Thermodynamics Research Center, College Station, **1994**.

[21] W. Tsang in *Energetics of Organic Free Radicals* (Eds.: J. A. Martinho Simões, A. Greenberg, J. F. Liebman), Blackie, London, **1996**, Chapter 2.

[22] D. Yu, A. Rauk, D. A. Armstrong, *J. Chem. Soc. Perkin Trans. 2* **1994**, *31*, 2207–2215.

[23] G. Leroy, M. Sana, C. Wilante, *J. Mol. Struct. (THEOCHEM)* **1991**, *228*, 37–45.

[24] P. G. Wenthold, R. R. Squires, *J. Am. Chem. Soc.* **1994**, *116*, 11890–11897.

[25] V. M. Orlov, A. D. Misharev, V. V. Takhistov, I. I. Ryabinkin, *Iz. Akad. Nauk. SSSR Ser. Khim.* **1988**, *7*, 1514–1515.

[26] J. L. Holmes, F. P. Lossing, P. M. Mayer, *J. Am. Chem. Soc.* **1991**, *113*, 9723–9728.

[27] J. Berkowitz, G. B. Ellison, D. Gutman, *J. Phys. Chem.* **1994**, *98*, 2744–2765.

[28] M. A. V. Ribeiro da Silva, M. J. S. Monte, J. R. Ribeiro, *J. Chem. Thermodyn.* **1999**, *31*, 1093–1107.

[29] a) A. R. Dias, J. A. Martinho Simões, C. Teixeira, C. Airoldi, A. P. Chagas *J. Organometal. Chem.* **1987**, *335*, 71–83; b) A. R. Dias, J. A. Martinho Simões, C. Teixeira, C. Airoldi, A. P. Chagas, *Polyhedron* **1991**, *10*, 1433–1441; c) J. A. Martinho Simões in *Energetics of Organometallic*, *Vol. 367* (Ed.: J. A. Martinho Simões), NATO Science Series C, Kluwer, Dordrecht, **1992**, Chapter 13; d) J. A. Martinho Simões, M. E. Minas da Piedade in *Energetics of Organic Free Radicals* (Eds.: J. A. Martinho Simões, A. Greenberg, J. F. Liebman), Blackie, London, **1996**, Chapter 6.

[30] H. E. Bryndza, L. K. Fong, R. A. Paciello, W. Tam, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 1444–1456.

[31] L. E. Schock, T. J. Marks, *J. Am. Chem. Soc.* **1988**, *110*, 7701–7715.

[32] J. W. Ochterski, G. A. Petersson, K. B. Wiberg, *J. Am. Chem. Soc.* **1995**, *117*, 11299–11308.

[33] C. A. Coulson, *Valence*, 2nd ed., Oxford University Press, New York, **1961**, p. 208–211.

[34] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, New York, **1960**, p. 92.

[35] a) S. G. Bratsch, *J. Chem. Educ.* **1988**, *65*, 34–41; b) S. G. Bratsch, *J. Chem. Educ.* **1988**, *65*, 223–227.

[36] The electronegativity of the $CH_2COOH$ group was calculated in this work by the method described in ref. [35].

[37] T. M. V. R. de Barros, R. C. Santos, A. C. Fernandes, M. E. Minas da Piedade, *Thermochim. Acta* **1995**, *269/270*, 51–60.

[38] a) J. C. G. Calado, A. R. Dias, M. E. Minas da Piedade, J. A. Martinho Simões, *Rev. Port. Quim.* **1980**, *22*, 53–62; b) H. P. Diogo, M. E. Minas da Piedade, A. C. Fernandes, J. A. Martinho Simões, M. A. V. Ribeiro da Silva, M. J. S. Monte, *Thermochim. Acta* **1993**, *228*, 15–22.

[39] a) M. A. V. Ribeiro da Silva, M. L. C. C. H. Ferrão, A. J. M. Lopes, *J. Chem. Thermodyn.* **1993**, *25*, 229–235; b) M. A. V. Ribeiro da Silva, M. L. C. C. H. Ferrão, F. Jiye, *J. Chem. Thermodyn.* **1994**, *26*, 839–846; c) M. A. V. Ribeiro da Silva, M. L. C. C. H. Ferrão, A. M. R. O. Alves da Silva, *J. Chem. Thermodyn.* **1995**, *27*, 633–641.

[40] L. Bjellerup in *Experimental Thermochemistry*, *Vol. 2* (Ed.: H. A. Skinner), Wiley, New York, **1962**, Chapter 3.

[41] L. Smith, L. Bjellerup in *Experimental Thermochemistry*, *Vol. 1* (Ed.: F. D. Rossini), Wiley, New York, **1956**, Chapter 9.

[42] A. S. Carson, P. G. Laye, J. B. Pedley, A. M. Welsby, *J. Chem. Thermodyn.* **1993**, *25*, 262–269.

[43] a) W. D. Good, D. W. Scott, G. Waddington, *J. Phys. Chem.* **1956**, *60*, 1080–1089; b) S. R. Gunn, *J. Chem. Thermodyn.* **1971**, *3*, 19–34.

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

[45] *Gaussian 94*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Peterson, J. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Repogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFreees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian Inc., Pittsburgh PA, **1995**.

[46] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[47] J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244–13249.

[48] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[49] J. S. Binkley, J. A. Pople, W. J. Hehre, *J. Am. Chem. Soc.* **1980**, *102*, 939–950.

[50] P. C. Hariharan, J. A. Pople, *Mol. Phys.* **1974**, *27*, 209–214.

[51] A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648.

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