Energetics of the C−Cl Bond in $CH_3CH(Cl)COOH$. Enthalpy of Formation of (*S*)-(−)-2-Chloropropionic Acid and of the 1-Carboxyethyl Radical[†,‡]

Ana L. C. Lagoa, Hermínio P. Diogo, and Manuel E. Minas da Piedade*

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

Luísa M. P. F. Amaral

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

Rita C. Guedes and Benedito J. Costa Cabral[§]

Centro de Física da Matéria Condensada da Universidade de Lisboa and Departamento de Química e
Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1649-016 Lisboa, Portugal

Dmitry V. Kulikov and Sergey P. Verevkin[||]

Department of Physical Chemistry, University of Rostock, Hermannstrasse 14, 18051 Rostock, Germany

Michael Siedler and Matthias Epple[⊥]

Solid State Chemistry, Faculty of Chemistry, University of Bochum, D-44780 Bochum, Germany

Received: February 12, 2002; In Final Form: May 13, 2002

The energetics of the C−Cl bond in 2-chloropropionic acid was investigated by using a combination of experimental and theoretical methods. The standard molar enthalpy of formation of liquid (*S*)-(−)-2-chloropropionic acid, at 298.15 K, was determined as $\Delta_f H^\circ_m(C_3H_5O_2Cl, l) = -(534.6 \pm 1.1)$ kJ·mol^{-1}, by rotating-bomb combustion calorimetry. The corresponding enthalpy of vaporization, $\Delta_{vap} H^\circ_m(C_3H_5O_2Cl) = (64.9 \pm 0.5)$ kJ·mol^{-1}, was also obtained from vapor pressure versus temperature measurements by the transpiration method, leading to $\Delta_f H^\circ_m(C_3H_5O_2Cl, g) = -(469.7 \pm 1.2)$ kJ·mol^{-1}. This value, together with the enthalpy of the isodesmic and isogyric gas-phase reaction $CH_3CH(X)COOH(g) + C_2H_5(g) \rightarrow CH_3CHCOOH(g) + C_2H_5X(g)$ (X = H, Cl) predicted by density functional theory calculations and other auxiliary data, was used to derive the enthalpy of formation of the gaseous 1-carboxyethyl radical as $\Delta_f H^\circ_m[CH(CH_3)COOH, g] = -(293 \pm 3)$ kJ·mol^{-1}, from which $DH^\circ[H-CH(CH_3)COOH] = 380.7 \pm 3.9$ kJ·mol^{-1} and $DH^\circ[Cl-CH(CH_3)COOH] = 298.0 \pm 3.2$ kJ·mol^{-1} were obtained. These values are compared with the corresponding C−H and C−Cl bond dissociation enthalpies in XCH_2COOH, XCH_3, XC_2H_5, XCH_2Cl, $XCH(CH_3)Cl$, $XCH{=}CH_2$, and XC_6H_5 (X = H, Cl). The order $DH^\circ(C-H) > DH^\circ(C-Cl)$ is observed for the carboxylic acids and all other RX compounds. Comparison of $DH^\circ[X-CH(CH_3)COOH]$ and $DH^\circ[X-CH_2COOH]$ (X = H, Cl) indicates that the replacement of a hydrogen of the CH_2 group of XCH_2COOH by a methyl group leads to a decrease of both the C−H and C−Cl bond dissociation enthalpy. It is finally concluded that the major qualitative trends exhibited by the C−Cl bond dissociation enthalpies for the series of compounds addressed in this work can be predicted based on Pauling's electrostatic−covalent model.

Introduction

A considerable number of applications of halocarboxylic acids in laboratory synthesis and in industry are related to reactions in which the carbon−halogen bond is cleaved.[1,2] Among the halocarboxylic acids, the chloro derivatives are by far the most widely used. Surprisingly, very little information exists on the energetics of the carbon−chlorine bond in chlorocarboxylic acids,[3] as well as on the enthalpies of formation of the acids themselves[3−5] and of the radicals formed upon cleavage of the C−Cl bond.[3,6−8] These data are usually very helpful in the rationalization of the observed reactivity trends and in devising strategies for the synthesis of new compounds. In addition, they are important to model the pyrolysis[9,10] and the atmospheric chemistry of chlorocarboxylic acids. These two topics have become particularly relevant in recent years in relation to the environmental problems associated with the incineration of chlorinated organic compounds and with the suggestion that industrial sources of chlorine lead to the depletion of the ozone layer.[11] We have recently applied a combination of experimental

---

[†] Part of the special issue "Jack Beauchamp Festschrift".

[‡] This article is dedicated to Professor Jack L. Beauchamp on the occasion of his 60th birthday.

* Corresponding author: e-mail pcmemp@popsrv.ist.utl.pt.

[§] E-mail ben@adonis.cii.fc.ul.pt.

[||] E-mail sergey.verevkin@chemie.uni-rostock.de.

[⊥] E-mail matthias.epple@ruhr-uni-bochum.de.

10.1021/jp020412p CCC: $22.00

(combustion calorimetry, differential scanning calorimetry, and vapor pressure versus temperature measurements) and computational chemistry (density functional theory, DFT) methods to study the energetics of chloro-, bromo-, and iodoacetic acids and of the carboxymethyl radical.[3] Here, these studies are extended to chloropropionic acid and the 1-carboxyethyl radical.

Methods

Elemental analyses were carried out on a Heraeus XHN-O-Rapid analyzer. The optical rotation measurements were made on a Perkin-Elmer 341 polarimeter. The IR spectra were recorded on a Perkin-Elmer PE 1720 apparatus with NaCl plates. The ^{1}H and ^{13}C NMR spectra were obtained at ambient temperature on a Bruker AMX (400 MHz) spectrometer. The ^{13}C spectra were recorded at 75.5 MHz. Chemical shifts relative to tetramethylsilane (TMS) were calculated with $CHCl_3$ as an internal standard. Differential scanning calorimetry (DSC) measurements were made with a 2920 MTDSC temperature-modulated apparatus from TA Instruments. The apparatus was connected to a liquid nitrogen cooling accessory and was operated as a conventional DSC.

Materials. (*S*)-(−)-2-Chloropropionic acid was prepared from optically pure (*S*)−(+)-alanine (Merck 816000) by the method of Fu et al.[12] An amount of 50.0 g (0.56 mol) of (*S*)-(+)-alanine was dissolved in 750 cm^3 of HCl(aq, 6 mol·dm^{-3}), and the solution was cooled to 273 K. With stirring, 62.5 g (0.91 mol) of freshly pulverized sodium nitrite were added in small portions and at such a rate that the temperature of the solution remained between 273 and 278 K. About 2.5 h was required for this purpose, and the stirring was continued at 273 K for another 4 h. The resulting solution was extracted five times with 150 cm^3 diethyl ether portions. The ethereal extract was dried over $CaCl_2$ for 10 h, and the solvent was removed by evaporation. The slightly yellow residual liquid was fractionally distilled twice at 100 Pa and 329 K. After distillation, 26.4 g of colorless liquid (*S*)-(−)-2-chloropropionic acid was obtained, which corresponds to a yield of 43% (lit. 43.5%[12]). Polarimetric analysis (l = 10 cm, pure): $\alpha_D^{25} = -17.48°$ (lit. = $-18.2°$ [12]). IR (NaCl): $\tilde{\nu}$/cm^{-1} = 2993, 2933 (C−H), 1729 (COO$^-$), 1445, 1420 (COO$^-$, C−H), 1383, 1289, 1256, 1212, 1076, 990, 921, 858. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): $\delta = 1.73$ (d, $J = 7.12$ Hz, 3 H, CH_3), $\delta = 4.46$ (q, $J = 7.12$, 1 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$/TMS): $\delta = 21.40$ (s, CH_3), $\delta = 52.41$ (s, CH), $\delta = 176.36$ (s, COO). Elemental analysis for $C_3H_5O_2Cl$: expected C 33.20%, H 4.64%; found C 32.92%, H 4.83% (average of two measurements). The temperature of fusion of the sample obtained by DSC at the onset of the measuring curve was $T_{fus} = (266.2 \pm 1.2)$ K. The corresponding enthalpy of fusion was $\Delta_{fus}H^\circ_m(C_3H_5O_2Cl) = (9.8 \pm 0.3)$ kJ·mol^{-1}. The uncertainties quoted for both values represent twice the standard deviation of the mean of five independent determinations.

Heat Capacity Mesurements by DSC. The heat capacity of liquid (*S*)-(−)-2-chloropropionic acid was measured as recommended by Richardson.[13] This involved three sequential runs with the same scanning program and a heating rate of 10 K·min^{-1}: (i) the zero line run with two empty crucibles in the sample and reference holders; (ii) a second run, used to calibrate the heat flow scale of the apparatus in terms of heat capacity, with synthetic sapphire (α-Al_2O_3 pellets, NIST-RM 720) inside the sample crucible; and (iii) a third run performed by replacing sapphire by (*S*)-(−)-2-chloropropionic acid in the sample crucible. The temperature scale of the apparatus was calibrated by taking the onsets of the fusion peaks of the following compounds: *n*-decane, $T_{fus} = 243.75$ K; *n*-octadecane, $T_{fus} = 301.47$ K; hexatriacontane, $T_{fus} = 347.30$ K; indium, $T_{fus} = 430.61$ K; and tin, $T_{fus} = 506.03$ K. The organic standards were high-purity Fluka products, and the metal standards were supplied by TA Instruments Inc. The samples were sealed, under air, in aluminum pans and weighed to $\pm 10^{-7}$ g in a Mettler UMT2 ultramicro balance. Helium (Air Liquide N55) at a flow rate of 0.5 cm^3·s^{-1} was used as the purging gas.

Enthalpy of Vaporization Measurements by the Transpiration Method. The enthalpy of vaporization of (*S*)-(−)-2-chloropropionic acid was determined from vapor pressure versus temperature measurements by the transpiration method.[14] About 0.5 g of sample was mixed with glass beads and placed in a thermostated (±0.1 K) U-shaped glass tube of 20 cm length and 0.5 cm diameter. A nitrogen stream was passed through the U-tube at a flow rate of 0.946 or 0.960 cm^3·s^{-1}, and the transported amount of material was condensed in a cold trap kept at 243 K. The flow rate of nitrogen was measured with a soap bubble flow-meter and was maintained constant with help of a high-precision needle valve (Hoke, C1335G6 BMM-ITA). The mass of condensed product was determined by gas−liquid chromatography (GC) analysis with *n*-$C_{11}H_{24}$ as internal standard. These analyses were carried out on a Carlo Erba GC Fraktometer (Vega Series GC 6000), equipped with a SE-30 capillary column of 25 m length, a flame ionization detector (FID), and a Hewlett-Packard 3390A integrator. The injector and the detector were kept at 523 K, and the column was kept at 363 K. A nitrogen flow of 0.333 cm^3·s^{-1} was used as the carrier gas in the analysis. At the end of each transpiration run, 200 μL of a standard solution of *n*-$C_{11}H_{24}$ in CH_3CN of concentration 4.65 g·dm^{-3} was added to the trap containing the condensed (*S*)-(−)-2-chloropropionic acid, and 0.1 μL of the resulting mixture was injected in the GC apparatus. The corresponding mass of sample (m) was then obtained from $m/m_{st} = a + b(A/A_{st})$, where $m_{st} = 0.93$ mg is the mass of *n*-$C_{11}H_{24}$, A and A_{st} are the areas of the sample and the internal standard peaks, respectively, and a and b are constants previously found by calibration of the chromatographic apparatus by use of solutions with known amounts of (*S*)-(−)-2-chloropropionic acid and *n*-$C_{11}H_{24}$.

A critical aspect of the transpiration method is the selection of an adequate carrier gas flow rate across the saturation tube at the temperature of the experiment. The flow rate, q_V, must be low enough to allow the saturation of the nitrogen stream with the compound under study before exiting the U-tube. However, if the flow rate is too low, the transport of material out of the U-tube by diffusion may significantly compete with the transport by transpiration. Tests conducted on our apparatus with a variety of carboxylic acids and alcohols[14,15] indicated that the unsaturation and diffusion effects could be avoided provided a flow rate in the range 0.11 cm^3·s^{-1} $\leq q_V \leq$ 1.5 cm^3·s^{-1} was selected. In the present experiments, flow rates of 0.946 or 0.960 cm^3·s^{-1} were used.

Combustion Calorimetry. The isoperibol rotating-bomb combustion calorimeter used in this work has been described.[16] The bomb, with a volume of 0.258 dm^3, was of stainless steel lined with platinum, and all the internal fittings were machined 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 ca. 11.7 g. In a typical experiment, the liquid sample sealed inside a Melinex bag and the *n*-hexadecane (Aldrich, Gold Label) used as a combustion aid, were weighed 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 weighed 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. A volume of 20 cm^3 of a 0.09016 $mol \cdot dm^{-3}$ As_2O_3(aq) was placed inside the bomb. The presence of the arsenious oxide solution ensured that all Cl_2 formed in the combustion was reduced to aqueous HCl.[17,18] 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 with a Hewlett-Packard (HP2804A) quartz thermometer. The duration of the fore, main, and after periods was ca. 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.[19,20] The HNO_3 formed from traces of atmospheric N_2 remaining inside the bomb was analyzed by the Devarda's alloy method.[21] The extent of the reaction of Cl_2 formed in the combustion with the arsenious oxide solution was found by titrating the final bomb solution with sodium thiosulfate (0.100 $mol \cdot dm^{-3}$).[21]

Computational Details. The density functional theory (DFT) calculations reported in this study were carried out with the Gaussian-98 program.[22] The geometry optimizations and the calculations of the total energies were made by the Becke three-parameter hybrid method[23] with the Perdew and Wang PW91[24] correlation functional (B3PW91). This hybrid functional is known to predict accurate values for reaction enthalpies with moderately sized basis sets.[25] Total energies (E) were obtained from[26]

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

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 energies, respectively, functionals of the electronic density ρ. Full geometry optimizations have been carried out with the 6-31G(d,p),[27] 6-311+G(d,p),[28] and aug-cc-pVDZ[29] basis sets. The corresponding total energies were corrected with the zero-point vibrational energies (ZPVEs) and thermal energy corrections (without frequency scaling) calculated at the same theoretical level. Single-point energy calculations with the aug-cc-pVTZ[30] basis set based on geometries, zero-point energy, and thermal energy corrections obtained from the aug-cc-pVDZ basis set were also made.

TABLE 1: Results of Vapor Pressure Measurements on (*S*)-(−)-2-Chloropropionic Acid

m/mg	V_{N_2}/dm^3	T/K	p/Pa
3.670	6.280	287.4	13.36
3.366	4.379	290.5	17.54
3.373	3.428	293.4	22.42
4.161	3.124	296.3	30.31
5.221	3.008	299.5	39.47
4.899	2.215	302.5	50.26
5.738	1.988	305.4	65.57
5.247	1.440	308.4	82.72
4.041	0.879	311.4	104.4
3.497	0.605	314.4	131.2
3.111	0.461	316.4	153.2
3.411	0.403	319.3	191.9
4.190	0.398	322.3	238.9
3.673	0.284	325.3	293.4
3.610	0.231	328.3	355.3

Results and Discussion

The heat capacity of liquid (*S*)-(−)-2-chloropropionic acid obtained by DSC, at 298.15 K, was $C^{\circ}_{p,m}(C_3H_5O_2Cl, l) = (260 \pm 6)$ $J \cdot K^{-1} \cdot mol^{-1}$, where the uncertainty quoted represents twice the standard deviation of the mean of three independent results. This value is in agreement with $C^{\circ}_{p,m}(C_3H_5O_2Cl, l) = (252 \pm 25)$ $J \cdot K^{-1} \cdot mol^{-1}$ previously reported by Sano et al.[31] in the temperature range 318−333 K. It is also interesting to note that two widely used versions of the Kopp method lead to $C^{\circ}_{p,m}(C_3H_5O_2Cl, l) = 149$ and 209 $J \cdot K^{-1} \cdot mol^{-1}$, respectively.[32] These lower predictions probably reflect the inadequacy of the method to estimate $C^{\circ}_{p,m}$ of strongly associated liquids. The heat capacity of gaseous (*S*)-(−)-2-chloropropionic acid predicted by DFT calculations (B3PW91) with the 6-311+G(d,p) and aug-cc-pVDZ basis sets were 101.6 and 102.1 $J \cdot K^{-1} \cdot mol^{-1}$, respectively. The average of these two values, $C^{\circ}_{p,m}(C_3H_5O_2Cl, g) = 101.9$ $J \cdot K^{-1} \cdot mol^{-1}$, was selected in the present work.

The vapor pressures p of (*S*)-(−)-2-chloropropionic acid as a function of the temperature measured by the transpiration method are given in Table 1. These results were obtained by using the following iterative procedure. A first approximation of p (p_1) was calculated from the mass m of product collected within a definite time period:[14]

$$p = \frac{mRT_a}{MV_{N_2}} \qquad (2)$$

where $R = 8.31451$ $J \cdot K^{-1} \cdot mol^{-1}$ is the gas constant, M is the molar mass of the sample, $T_a = 296 \pm 1$ K is the ambient temperature, and V_{N_2} is the total volume of N_2 used as carrier gas throughout the experiment. The obtained results were fitted to the Clausius−Clapeyron equation

$$\ln p = a + \frac{b}{T} \qquad (3)$$

by the least-squares method, and the resulting equation was used to derive a first approximation of the residual pressure of the compound (p_{r1}) at the condensation temperature (243 K). New values of p were derived as $p_2 = p_1 + p_{r1}$. These were subsequently fitted to eq 3 and a second approximation of the residual pressure of the compound (p_{r2}) at the condensation temperature was computed. A third series of p values was calculated as $p_3 = p_1 + p_{r2}$ and the iteration was continued until the difference between successive values of p_r was smaller than 10^{-4} Pa.

Equation 2 is based on the assumption that N_2 and the vapor of (*S*)-(−)-2-chloropropionic acid constitute an ideal gas mixture

TABLE 2: Results of the Combustion Experiments on (*S*)-(−)-2-Chloropropionic Acid

$m(C_3H_5O_2Cl)$/g	0.751 36	0.744 81	0.853 54	0.840 12	0.769 25	0.792 62	0.790 81
m(cotton)/g	0.002 69	0.002 28	0.002 81	0.002 65	0.002 70	0.002 69	0.002 47
$m(n\text{-}C_{16}H_{34})$/g	0.302 26	0.299 59	0.295 15	0.303 57	0.302 17	0.294 68	0.301 97
m(Melinex)/g	0.044 94	0.042 06	0.045 09	0.044 59	0.041 13	0.050 03	0.045 58
$\Delta m(H_2O)$/g	1.7	0.8	1.5	1.3	−0.5	0.1	0.1
$10^5 \times n(HNO_3)$/mol	8.0	5.0	3.0	4.0	8.0	10.0	5.0
$10^4 \times n(As_2O_3)$/mol	5.02	4.09	4.69	4.75	4.09	4.36	4.12
$10^6 \times n(H_2PtCl_6)$/mol	2.08	2.12	3.18	1.67	2.52	2.24	1.59
$\epsilon_i/J \cdot K^{-1}$	94.95	94.93	95.11	95.10	94.97	95.01	95.01
$\epsilon_f/J \cdot K^{-1}$	93.52	93.56	93.56	93.60	93.61	93.59	93.61
T_i/K	297.1288	297.1480	297.0922	297.0840	297.1289	297.1288	297.1165
T_f/K	298.1398	298.1464	298.1420	298.1420	298.1446	298.1505	298.1460
ΔT_c/K	0.017 60	0.017 27	0.017 44	0.017 48	0.017 16	0.016 88	0.017 20
ΔU_{ign}/J	1.29	1.29	1.29	1.29	1.29	1.29	1.29
$-\Delta U_{IBP}$/J	25 112.41	24 799.00	26 098.11	26 301.23	25 232.66	25 393.15	25 583.72
ΔU_{Σ}/J	46.03	35.50	48.02	48.27	46.25	46.80	47.05
$\Delta U(HNO_3)$/J	4.78	2.98	1.79	2.39	4.78	5.97	2.98
$\Delta U(As_2O_3)$/J	160.68	130.93	150.12	152.36	130.93	139.56	131.88
$\Delta U(H_2PtCl_6)$/J	0.51	0.52	0.78	0.41	0.62	0.55	0.39
$\angle\Delta U$(Melinex)/J	1029.16	963.36	1032.58	1021.16	941.89	1145.89	1043.78
$-\Delta U$(cotton)/J	43.69	37.03	45.63	43.04	43.85	43.69	40.11
$-\Delta U(n\text{-}C_{16}H_{34})$/J	14 254.39	14 128.32	13 918.68	14 315.78	14 250.14	13 896.96	14 240.70
$\Delta U(C_3H_5O_2Cl)$/J	9573.17	9500.36	10 900.51	10 717.82	9814.20	10 113.73	10 076.83
$-\Delta_c u^o(C_3H_5O_2Cl)/J \cdot g^{-1}$	12 741.12	12 755.41	12 770.94	12 757.49	12 758.14	12 759.87	12 742.42

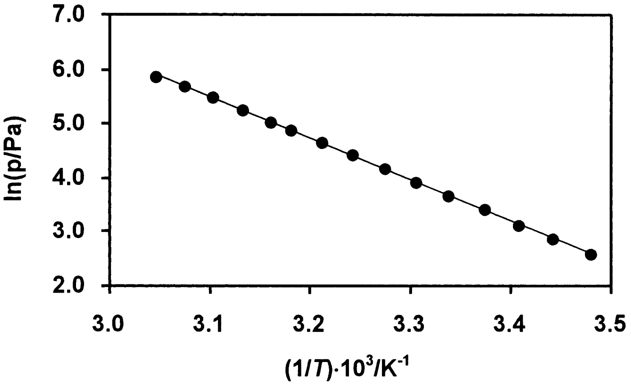

Figure 1. Vapor pressure of (*S*)-(−)-2-chloropropionic acid as a function of the temperature.

and that the total volume of the mixture is V_{N_2} (i.e., the volume of the acid is negligible). The values of V_{N_2} were determined from the selected flow rates and the duration of the experiments. The accuracy of the V_{N_2} measurements was established to be ± 0.001 dm^3 in a series of experiments where the nitrogen volume used was obtained with a gas-clock or with a calibrated gasometer. Because the nitrogen flow rate was measured with a soap bubble flow-meter at ambient temperature, this temperature was used in eq 2 for the calculation of p.

Least-squares fitting of eq 3 to the p vs T data in Table 1 lead to $a = (29.14 \pm 0.21)$ and $b = -\Delta_{vap}H^{\circ}_{m}/R = -(7629.8 \pm 65.7)$ K with a regression coefficient of 0.9999. The corresponding plot of ln p versus $1/T$ is presented in Figure 1. From these results, $\Delta_{vap}H^{\circ}_{m}(C_3H_5O_2Cl) = 63.4 \pm 0.5$ kJ·mol^{-1} at the mean temperature of the temperature range covered by the experiments, $T_m = 307.9$ K, is obtained. The uncertainties quoted for a and b and $\Delta_{vap}H^{\circ}_{m}(C_3H_5O_2Cl)$ values include Student's factor for 95% confidence level ($t = 2.145$).[33] The enthalpy of vaporization of (*S*)-(−)-2-chloropropionic acid at 298.15 K can be calculated from the corresponding value at 307.9 K and the heat capacity data indicated above:

$$\Delta_{vap}H^{\circ}_{m}(298.15\ K) = \Delta_{vap}H^{\circ}_{m}(307.9\ K) + \Delta_{vap}C^{\circ}_{p,m}(298.15\ K - 307.9\ K) \quad (4)$$

where $\Delta_{vap}C^{\circ}_{p,m}$ represents the difference in heat capacity of the gaseous and liquid compound. This leads to $\Delta_{vap}H^{\circ}_{m}(C_3H_5O_2Cl) = 64.9 \pm 0.5$ kJ·mol^{-1} at 298.15 K.

The results of the combustion calorimetric experiments are shown in Table 2, where $m(C_3H_5O_2Cl)$ is the mass of (*S*)-(−)-2-chloropropionic acid; m(cotton) represents the mass of the cotton thread fuse of empirical formula $CH_{1.686}O_{0.843}$; m(Melinex) is the mass of the Melinex bag containing the sample; $m(n\text{-}C_{16}H_{34})$ is the mass of n-hexadecane used as combustion auxiliary; $\Delta m(H_2O)$ represents the difference between the mass of water inside the calorimeter proper and the average mass of water used in the calibration experiments (5217.0 g); $n(HNO_3)$ is the amount of substance of nitric acid formed in the bomb process; $n(As_2O_3)$ is the amount of substance of arsenious oxide consumed in the reaction with the Cl_2; $n(H_2PtCl_6)$ is the amount of substance of H_2PtCl_6 formed in the bomb process from the mass of platinum lost by the crucible and its supporting ring; ϵ_i and ϵ_f are the energy equivalents of the bomb contents in the initial and final states of the bomb process, respectively; T_i and T_f represent the initial and final temperatures of the experiment; ΔT_c is the contribution to the observed temperature rise of the calorimeter proper due to the heat exchanged with the surroundings, the heat of stirring, and the heat dissipated by the temperature sensor and by the bomb rotation; ΔU_{ign} is the electrical energy supplied for ignition of the sample; ΔU_{IBP} is the internal energy change associated with the bomb process under isothermal conditions, at 298.15 K; ΔU_{Σ} represents the sum of all corrections necessary to reduce ΔU_{IBP} to the standard state (Washburn corrections); $\Delta U(HNO_3)$ is the energy change associated with the formation of nitric acid; $\Delta U(As_2O_3)$, is the energy change due to the reaction of the aqueous As_2O_3 inside the bomb with the Cl_2 formed in the combustion; $\Delta U(H_2PtCl_6)$ represents the energy change associated with the conversion of Pt to H_2PtCl_6, in the bomb process; ΔU(Melinex), ΔU(cotton), $\Delta U(n\text{-}C_{16}H_{34})$, and $\Delta U(C_3H_5O_2Cl)$ are the contributions of the Melinex container, cotton thread fuse, n-hexadecane, and (*S*)-(−)-2-chloropropionic acid, respectively, to the energy of the isothermal bomb process; and finally, $\Delta_c u^{\circ}(C_3H_5O_2Cl)$ is the standard specific energy of combustion of (*S*)-(−)-2-chloropropionic acid.

The molar masses used in the calculation of molar quantities are based on the 1995 standard atomic masses.[34] The values of

TABLE 3: Theoretically Calculated Enthalpies of Reaction 11 and Enthalpies of Formation of $CH(CH_3)COOH(g)$ at 298.15 K[a]

	X = H		X = Cl	
method	$-\Delta_r H^\circ_m(11)$	$-\Delta_f H^\circ_m[CH(CH_3)COOH, g]$	$-\Delta_r H^\circ_m(11)$	$-\Delta_f H^\circ_m[CH(CH_3)COOH, g]$
B3PW91/6-31G(d,p)	40.7	293.6	56.5	295.1
B3PW91/6-311+G(d,p)	37.5	290.4	54.4	293.0
B3PW91/aug-cc-pVDZ	36.7	289.6	54.7	293.3
B3PW91/aug-cc-pVTZ// B3PW91/aug-cc-pVDZ	38.0	290.9	55.5	294.1

[a] Data are given in kilojoules per mole.

T_i, T_f, and ΔT_c were calculated by using a computer program[35] based on the Regnault-Pfaundler method,[36−38] and ΔU_{IBP} was derived from[39]

$$\Delta_{IBP}U = [\epsilon_o + \Delta m(H_2O)C^\circ_{p,m}(H_2O, l)](T_i - T_f + \Delta T_c) + \epsilon_i(T_i - 298.15) + \epsilon_f(298.15 - T_f + \Delta T_c) + \Delta U_{ign} \quad (5)$$

The energy equivalent of the calorimeter and its standard deviation, $\epsilon_o = 25177.4 \pm 1.4$ J·K^{-1}, was determined, in the conventional way, without bomb rotation,[37,40,41] from the combustion of benzoic acid (Bureau of Analyzed Samples, Thermochemical Standard CRM-190r), whose energy of combustion under certificate conditions was −(26432.3 ± 3.8) J·g^{-1}. The standard state corrections, ΔU_Σ, were derived as recommended in the literature for organic compounds containing chlorine,[42,43] by using the following auxiliary data: for *n*-hexadecane, $c^\circ_p = 2.215$ J·K^{-1}·g^{-1},[44] $\rho = 0.773$ g·cm^{-3},[44] and $-(\partial u/\partial p)_T = 0.347$ J·MPa^{-1}·g^{-1};[45] for (*S*)-(−)-2-chloropropionic acid, $c^\circ_p = 2.396$ J·K^{-1}·g^{-1} (this work, see above), $\rho = 1.2585$ g·cm^{-3},[44] $-(\partial u/\partial p)_T = 0.20$ J·MPa^{1-}·g^{-1}.[46] The values of $\Delta U(HNO_3)$ and $\Delta U(H_2PtCl_6)$ correspond to the processes

$$HNO_3(aq,\ 0.1\ mol{\cdot}dm^{-3}) \rightarrow \frac{1}{2}H_2O(l) + \frac{1}{2}N_2(g) + \frac{5}{4}O_2(g) \quad (6)$$

$$H_2PtCl_6(aq) + 2H_2O(l) \rightarrow Pt(cr) + O_2(g) + 6HCl(aq) \quad (7)$$

and were obtained from the following data: $\Delta_f U^\circ_m(HNO_3$, aq, 0.1 mol·dm$^{-3}) = -59.7$ kJ·mol^{-1} [47] and $\Delta_r U^\circ_m(7) = 245.6$ kJ·mol^{-1}.[48] The term $\Delta U(As_2O_3)$, corresponds to

$$As_2O_5(aq) \rightarrow As_2O_3(aq) + O_2(aq) \quad (8)$$

It depends on the concentration of As_2O_5 and H^+ in the final bomb solution and was derived for each experiment by using the equations and data given by Hu et al.[42] The calculation of ΔU(cotton), and ΔU(Melinex) was based on $\Delta_c u^\circ$(cotton) = −16250 J·g^{-1} [39,49] and $\Delta_c u^\circ$(Melinex) = −(22902 ± 5) J·g^{-1}.[50] The values of $\Delta U(n\text{-}C_{16}H_{34})$ were obtained by using $\Delta_c u^\circ(n\text{-}C_{16}H_{34}) = -(47158.7 \pm 3.2)$ J·g^{-1},[51] which was independently measured by static-bomb combustion calorimetry. The standard specific energy of combustion of (*S*)-(−)-2-chloropropionic acid was calculated from

$$\Delta_c u^\circ(C_3H_5O_2Cl) = [\Delta U_{IBP} + \Delta U_\Sigma + \Delta U(HNO_3) + \Delta U(As_2O_3) + \Delta U(H_2PtCl_6) - \Delta U(\text{cotton}) - \Delta U(n\text{-}C_{16}H_{34}) - \Delta U(\text{Melinex})]/m(C_3H_5O_2Cl) \quad (9)$$

The mean value of the standard massic energies of combustion of (*S*)-(−)-2-chloropropionic acid indicated in Table 2 is $\Delta_c u^\circ(C_3H_5O_2Cl) = -(12755.06 \pm 3.92)$ J·g^{-1}, where the uncertainty quoted is the standard deviation of the mean. This result refers to

$$C_3H_5O_2Cl\ (l) + 3O_2\ (g) + 598H_2O\ (l) \rightarrow 3CO_2\ (g) + HCl{\cdot}600H_2O\ (l) \quad (10)$$

and leads to $\Delta_c U^\circ_m = \Delta_c H^\circ_m = -(1384.22 \pm 1.04)$ kJ·mol^{-1}. The uncertainties quoted represent twice the overall standard deviation of the mean and include the contributions from the calibration with benzoic acid and from the energy of combustion of *n*-hexadecane.[52] From the $\Delta_c H^\circ_m$ value indicated above and $\Delta_f H^\circ_m(CO_2, g) = -(393.51 \pm 0.13)$ kJ·mol^{-1},[53] $\Delta_f H^\circ_m(H_2O, l) = -(285.830 \pm 0.040)$ kJ·mol^{-1},[53] and $\Delta_f H^\circ_m(HCl{\cdot}600H_2O, l) = -(166.619)$ kJ·mol^{-1},[47] it is possible to derive $\Delta_f H^\circ_m(C_3H_5O_2Cl, l) = -(534.6 \pm 1.1)$ kJ·mol^{-1}. This value differs by 10.9 kJ·mol^{-1} from $\Delta_f H^\circ_m(C_3H_5O_2Cl, l) = -(523.7 \pm 8.3)$ kJ·mol^{-1},[4,5] previously measured by Smith et al.[4] using static bomb combustion calorimetry, which, in principle, does not yield reliable results for chlorine-containing organic compounds.[17,19,54,55] The enthalpy of formation of liquid (*S*)-(−)-2-chloropropionic acid and the corresponding enthalpy of vaporization obtained in this work lead to $\Delta_f H^\circ_m(C_3H_5O_2Cl, g) = -(469.7 \pm 1.2)$ kJ·mol^{-1}.

The standard enthalpy of formation of the $CH(CH_3)COOH$ radical was derived from the enthalpy of the isodesmic and isogyric reaction 11, $\Delta_r H^\circ_m(11)$, calculated by DFT for X = H, Cl (Table 3). The $\Delta_f H^\circ_m[CH(CH_3)COOH, g]$ values in Table 3 were obtained through eq 12 by using the enthalpy of formation of gaseous $ClCH(CH_3)COOH$ determined in this work (−469.7 ± 1.2 kJ·mol^{-1}) and $\Delta_f H^\circ_m(CH_3CH_2COOH, g) = -(455.7 \pm 2.5)$ kJ·mol^{-1},[5] $\Delta_f H^\circ_m(C_2H_6, g) = -(83.8 \pm 0.3)$ kJ·mol^{-1},[5] $\Delta_f H^\circ_m(C_2H_5Cl, g) = -(112.1 \pm 1.1)$ kJ·mol^{-1},[5] and $\Delta_f H^\circ_m(C_2H_5, g) = 119 \pm 2$ kJ·mol^{-1}.[56]

$$XCH(CH_3)COOH(g) + C_2H_5(g) \rightarrow CH(CH_3)COOH(g) + C_2H_5X(g) \quad (11)$$

$$\Delta_f H^\circ_m[CH(CH_3)COOH, g] = \Delta_r H^\circ_m(11) - \Delta_f H^\circ_m(C_2H_5X, g) + \Delta_f H^\circ_m(C_2H_5, g) + \Delta_f H^\circ_m[XCH(CH_3)COOH, g] \quad (12)$$

As seen in Table 3, the $\Delta_r H^\circ_m(11)$ results are quite insensitive to the basis set used in the calculation. In addition, the values of $\Delta_f H^\circ_m[CH(CH_3)COOH, g]$ obtained from the several $\Delta_r H^\circ_m(11)$ results and the auxiliary enthalpy of formation data indicated above 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 $\Delta_f H^\circ_m[CH(CH_3)COOH, g]$, −(293 ± 3) kJ·mol^{-1}, is the mean of the results in Table 3. This value, together with $\Delta_f H^\circ_m(H, g) = 217.998 \pm 0.006$ kJ·mol^{-1},[53] $\Delta_f H^\circ_m(Cl, g) = 121.301 \pm 0.008$ kJ·mol^{-1},[53] and

TABLE 4: R−X Bond Dissociation Enthalpies in kJ·mol^{-1}

	X		
R	H (2.25)	Cl (3.10)	R
CH_2COOH (2.74)	412.8 ± 3.2^b	310.9 ± 2.2^b	342.7 ± 4.3^b
$CH(CH_3)COOH$ (2.61)	380.7 ± 3.9^c	298.0 ± 3.2^c	279.1 ± 6.7^d
CH_3 (2.31)	438.8 ± 0.6^b	349.6 ± 0.6^b	376.6 ± 0.6^b
C_2H_5 (2.32)	420.8 ± 2.0^b	352.4 ± 2.3^b	363.7 ± 2.9^b
CH_2Cl (2.55)	418.9 ± 2.5^e	335.7 ± 2.6^e	364.6 ± 5.3^d
$CH(CH_3)Cl$ (2.46)	406.5 ± 2.2^e	324.5 ± 2.4^e	
$CH{=}CH_2$ (2.43)	465.1 ± 3.3^b	400.0 ± 5.3^e	489.2 ± 4.8^b
C_6H_5 (2.49)	465.5 ± 3.5^b	399.4 ± 1.7^b	478.8 ± 5.1^b

[a] Enthalpies are given in kilocalories per mole. Pauling's electronegativities[60] of the R and X fragments are given in parentheses. [b] Reference 3. [c] This work. [d] Reference 59. [e] Reference 57.

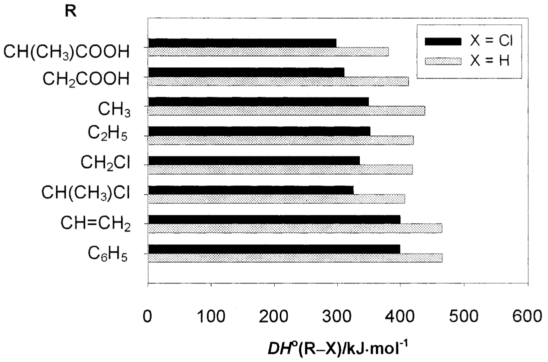

Figure 2. R−H and R−Cl bond dissociation enthalpies.

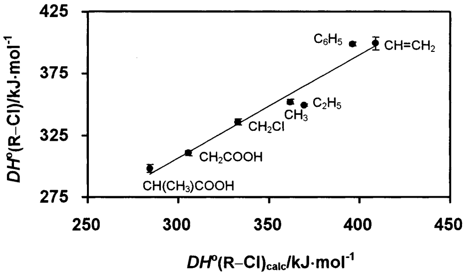

Figure 3. Experimental R−Cl bond dissociation enthalpies, DH°(R−Cl), from Table 4, versus the corresponding values calculated from eq 13, $DH^\circ(\mathrm{R{-}Cl})_{calc}$, for R = CH_2COOH, $CH(CH_3)COOH$, CH_3, C_2H_5, CH_2Cl, $CH(CH_3)Cl$, $CH{=}CH_2$, and C_6H_5.

the standard enthalpies of formation of $\Delta_f H^\circ_m[XCH(CH_3)COOH, g]$ (X = H, Cl) indicated above, yield the bond dissociation enthalpies $DH^\circ[H{-}CH(CH_3)COOH] = 380.7 \pm 3.9$ kJ·mol^{-1} and $DH^\circ[Cl{-}CH(CH_3)COOH] = 298.0 \pm 3.2$ kJ·mol^{-1}. These values are compared in Table 4 with the corresponding C−H and C−Cl bond dissociation enthalpies in XCH_2COOH, XCH_3, XC_2H_5, XCH_2Cl, $XCH(CH_3)Cl$, $XCH{=}CH_2$, and XC_6H_5 (X = H, Cl) quoted or calculated from the literature.[3,57] The order $DH^\circ(C{-}H) > DH^\circ(C{-}Cl)$ is observed for the carboxylic acids and all other RX compounds in Table 4 (Figure 2). Comparison of $DH^\circ[X{-}CH(CH_3)COOH]$ and $DH^\circ[X{-}CH_2COOH]$ (X = H, Cl) indicates that the replacement of a hydrogen of the CH_2 group of XCH_2COOH by a methyl group leads to a decrease of both the C−H and C−Cl bond dissociation enthalpy. This seems to be a general trend for $DH^\circ(C{-}H)$,[8] and $DH^\circ(C{-}Cl)$ with the notable exception $DH^\circ(Cl{-}CH_3) \lesssim DH^\circ(Cl{-}C_2H_5)$ (Table 4).

The major qualitative trends exhibited by the C−Cl bond dissociation enthalpies in Table 4 can be predicted on the basis of Pauling's electrostatic−covalent model.[58] As shown in Figure 3, there is a good linear correlation between the experimental DH°(R−Cl) values in Table 4 and the corresponding $DH^\circ(\mathrm{R{-}Cl})_{calc}$ values calculated from Pauling's arithmetic mean expression:

$$DH^\circ(\mathrm{R{-}Cl}) = \frac{DH^\circ(\mathrm{R{-}R}) + DH^\circ(\mathrm{C{-}Cl})}{2} + 96.232(\chi_R - \chi_{Cl})^2 \quad (13)$$

where $\chi_{Cl} = 3.10$ and χ_R are the electronegativities of Cl and R, respectively, by using $DH^\circ(\mathrm{Cl{-}Cl}) = 242.602 \pm 0.011$ kJ·mol^{-1} and the DH°(R−R)[3,59] and group electronegativity[60] data given in Table 4, respectively. This correlation corresponds to

$$DH^\circ(\mathrm{R{-}Cl}) = (0.833 \pm 0.083)DH^\circ(\mathrm{R{-}Cl})_{calc} + (56.87 \pm 29.48) \quad (14)$$

with a regression coefficient of 0.98. The average error in the estimation of DH°(R−Cl) from eq 14 is 8.8 kJ·mol^{-1}.

Finally, the results obtained in this work allow us to address the energetics of the gas-phase decompositions of chloroacetic and 2-chloropropionic acid, which are known to occur according to (R = H, CH_3)[9]

$$RCH(Cl)COOH(g) \rightarrow RCHO(g) + CO(g) + HCl(g) \quad (15)$$

From the enthalpy of formation of gaseous 2-chloropropionic acid determined in this work (−469.7 ± 1.2 kJ·mol^{-1}), $\Delta_f H^\circ_m(ClCH_2COOH, g) = -(427.55 \pm 1.04)$ kJ·mol^{-1},[3] $\Delta_f H^\circ_m(CO, g) = -(110.52 \pm 0.17)$ kJ·mol^{-1},[53] $\Delta_f H^\circ_m(HCl, g) = -(92.31 \pm 0.10)$ kJ·mol^{-1},[53] $\Delta_f H^\circ_m(HCHO, g) = -(108.6 \pm 0.5)$ kJ·mol^{-1},[5] and $\Delta_f H^\circ_m(CH_3CHO, g) = -(166.1 \pm 0.5)$ kJ·mol^{-1},[5] it is possible to conclude that $\Delta_r H^\circ_m(15) = 116.1 \pm 1.3$ kJ·mol^{-1} (R = H) and 100.8 ± 1.3 kJ·mol^{-1} (R = CH_3). In their theoretical study of the kinetics and mechanism of the thermal decomposition of 2-chloropropionic acid, Safont et al.[10] predicted the reaction to be endothermic with a computed reaction enthalpy noticeably dependent on the method of calculation: 80.42 kJ·mol^{-1} (MP2/6-31G**), 82.80 (MP2/6-31++G**), and 65.53 kJ·mol^{-1} (CISD/6-31G**) with a scale factor of 0.91, or 77.64 kJ·mol^{-1} (MP2/6-31G**), 80.03 (MP2/6-31++G**), and 62.61 kJ·mol^{-1} (CISD/6-31G**) without scale factor. Thus the calculations by Safont et al. correctly predict the reaction to be endothermic but the computed values are smaller than the experimental $\Delta_r H^\circ_m(15)$ value by 18−38 kJ·mol^{-1}.

Acknowledgment. This work was supported by Fundação para a Ciência e a Tecnologia (Project POCTI/199/QUI/35406), the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and Acções Integradas Luso-Alemãs. A Ph.D. grant from Fundação para a Ciência e a Tecnologia (PRAXIS XXI/BD/15920/98) is also gratefully acknowledged by R.C.G.

References and Notes

(1) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley: New York, 1992; p 412.

(2) *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed.; VCH: Weinheim, Germany, 1986.

(3) 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.

(4) Smith, L.; Bjellerup, L.; Krook, S.; Westermark, H. *Acta Chem. Scand.* **1953**, *7*, 65.

(5) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994; Vol. 1.

(6) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

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

(8) Kerr, J. A.; Stocker, D. W. In *Handbook of Chemistry and Physics*, 80th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1999−2000; Sect. 9.

(9) (a) Chuchani, G.; Rotinov, A. *Int. J. Chem. Kinet.* **1989**, *21*, 367. (b) Chuchani, G.; Martin, I.; Rotinov, A.; Dominguez, R. M.; Perez, I. M. *J. Phys. Org. Chem.* **1995**, *8*, 133.

(10) Safont, V. M.; Andrés, J.; Domingo, L. R. *J. Phys. Chem. A* **1997**, *101*, 1859.

(11) For a review and leading references, see *Stratospheric Ozone Depletion*; http://www.nas.nasa.gov/about/education/ozone.

(12) Fu, S.-C. J.; Birnbaum, M.; Greenstein, J. P. *J. Am. Chem. Soc.* **1954**, *76*, 6056.

(13) Richardson, M. J. In *Compendium of Thermophysical Properties Measurement Methods*; Maglic, K. D., Cezairliyan, A., Peletsky, V. E., Eds.; Plenum: New York, 1992; Vol. 2, Chapt. 18.

(14) Verevkin, S. P. *J. Chem. Eng. Data* **2000**, *45*, 953.

(15) Kulikov, D.; Verevkin, S. P.; Heintz, A. *J. Chem. Eng. Data* **2001**, *46*, 1593.

(16) (a) Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Lopes, A. J. M. *J. Chem. Thermodynamics* **1993**, *25*, 229. (b) Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Jiye, F. *J. Chem. Thermodynamics* **1994**, *26*, 839. (c) Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Alves da Silva, A. M. R. O. *J. Chem. Thermodynamics* **1995**, *27*, 633.

(17) Smith, L.; Hubbard, W. N. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapt. 8.

(18) Minas da Piedade, M. E. In *Energetics of Stable Molecules and Reactive Intermediates*; Minas da Piedade, M. E., Ed.; NATO Science Series C; Kluwer: Dordrecht, The Netherlands, 1999; Vol. 535, Chapt. 2.

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

(20) Gunn, S. R. *J. Chem. Thermodynamics* **1971**, *3*, 19.

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

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(23) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(24) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(25) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley−VCH: Weinheim, Germany, 2001.

(26) Parr, R.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; International Series of Monographs on Chemistry 16; Oxford University Press: Oxford, U.K., 1989.

(27) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209.

(28) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(29) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(30) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(31) Sano, T.; Tatsumoto, N.; Mende, Y.; Yasunaga, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2673.

(32) Hurst, J. E., Jr.; Harrison, B. K. *Chem. Eng. Commun.* **1992**, *112*, 21.

(33) Korn, G. A.; Korn, T. M. *Mathematical Handbook for Scientists and Engineers*; McGraw-Hill: New York, 1968.

(34) IUPAC, *J. Phys. Chem. Ref. Data* **1997**, *26*, 1239.

(35) LABTERMO, in Santos, L. M. N. B. F. *Tese de Doutoramento*; FCUP: Porto, Portugal, 1995.

(36) Cordfunke, E. H. P.; Ouweltjes, W. In *Experimental Thermodynamics, Volume IV*: *Solution Calorimetry*; Marsh, K. N., O'Hare, P. A. G., Eds.; Blackwell Scientific Publications: Oxford, U.K., 1994; Chapt. 14.

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

(38) Mosselman, C.; Churney, K. L. In *Experimental Chemical Thermodynamics*; Sunner, S., Månsson, M., Eds.; Pergamon Press: London, 1979; Vol. 1, Chapt. 3.

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

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

(41) (a) Jessup, R. S. *J. Res. Nat. Bur. Stand.* **1942**, *29*, 247. (b) *Recommended Reference Materials for the Realization of Physicochemical Properties*; Marsh, K. N., Ed.; IUPAC−Blackwell Scientific Publications: Oxford, U.K., 1987.

(42) Hu, A. T.; Sinke, G. C.; Månsson, M.; Ringnér, B. *J. Chem. Thermodynamics* **1972**, *4*, 283.

(43) Bjellerup, L. In *Experimental Thermochemistry*; Skinner, H. A., Ed.; Interscience: New York, 1962; Vol. 2, Chapt. 3.

(44) *Handbook of Chemistry and Physics*, 80th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1999−2000.

(45) Vargaftik, N. B. *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd ed.; John Wiley: New York, 1975.

(46) Calculated as $(\partial u/\partial p)_\mathrm{T} \approx -T(\partial V/\partial p)_\mathrm{T}$ by using the density data for (*S*)-(−)-2-chloropropionic acid reported in ref 31.

(47) 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*, Supplement 2.

(48) $\Delta_\mathrm{r}U^\circ_\mathrm{m}(7) = \Delta_\mathrm{r}H^\circ_\mathrm{m}(7) - RT = -245.6\ \mathrm{kJ{\cdot}mol^{-1}}$ (at 298.15 K) was based on $\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{H_2PtCl_6, aq}) = -676.1\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{HCl{\cdot}600H_2O}) = -166.619\ \mathrm{kJ{\cdot}mol^{-1}}$ given in ref 47.

(49) Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Costa, I. M. S. *J. Chem. Thermodynamics* **1999**, *31*, 1635.

(50) Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1960**, *56*, 1776.

(51) Amaral, L. M. P. F.; Ribeiro da Silva, M. A. V. Unpublished results.

(52) (a) Olofsson, G. In *Experimental Chemical Thermodynamics*; Sunner, S., Månsson, M., Eds.; Pergamon Press: London, 1979; Vol. 1, Chapt. 6. (b) Bjellerup, L. *Acta Chem. Scand.* **1961**, *15*, 121.

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

(54) Head, A. J.; Good W. D. In *Experimental Chemical Thermodynamics*; Sunner, S., Månsson, M., Eds.; Pergamon Press: London, 1979; Vol. 1, Chapt. 9.

(55) Hajiev, S. N. In *Thermochemistry and Equilibria of Organic Compounds*, Book I; Frenkel, M., Ed.; VCH: New York, 1993; Chapt. 4.

(56) Tsang, W. In *Energetics of Organic Free Radicals*; Martinho Simões, J. A., Greenberg, A., Liebman, J. F., Eds.; Blackie: London, 1996; Chapter 2.

(57) $DH^\circ(\mathrm{H{-}CH_2Cl}) = 418.9 \pm 2.5\ \mathrm{kJ{\cdot}mol^{-1}}$, $DH^\circ[\mathrm{H{-}CH_2(CH_3)Cl}] = 406.5 \pm 2.2\ \mathrm{kJ{\cdot}mol^{-1}}$, $DH^\circ(\mathrm{Cl{-}CH_2Cl}) = 335.7 \pm 2.6\ \mathrm{kJ{\cdot}mol^{-1}}$, and $DH^\circ[\mathrm{Cl{-}CH_2(CH_3)Cl}] = 325.4 \pm 2.4\ \mathrm{kJ{\cdot}mol^{-1}}$ were derived as follows. First $\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{CH_2Cl, g}) = 119.0 \pm 2.4\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_\mathrm{f}H^\circ_\mathrm{m}[\mathrm{CH_2(CH_3)Cl, g}] = 76.4 \pm 1.9\ \mathrm{kJ{\cdot}mol^{-1}}$ were obtained from $\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{CH_3Cl, g}) = -(81.9 \pm 0.5)\ \mathrm{kJ{\cdot}mol^{-1}}$ (ref 5), $\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{CH_3CH_2Cl, g}) = -(112.1 \pm 1.1)\ \mathrm{kJ{\cdot}mol^{-1}}$ (ref 5), $\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{HBr, g}) = -(36.29 \pm 0.16)\ \mathrm{kJ{\cdot}mol^{-1}}$ (ref 53), $\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{Br, g}) = 111.87 \pm 0.12\ \mathrm{kJ{\cdot}mol^{-1}}$ (ref 53), and the enthalpies of the reaction $\mathrm{RCHCl(g) + HBr(g) \rightarrow RCH_2Cl(g) + Br(g)}$ ($-52.7 \pm 2.3\ \mathrm{kJ{\cdot}mol^{-1}}$ for R = H and $-40.3 \pm 1.5\ \mathrm{kJ{\cdot}mol^{-1}}$, for R = CH_3) reported in Seetula, J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3069. Then the above-mentioned bond dissociation enthalpies were computed by using $\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{CH_2Cl_2, g}) = -(95.4 \pm 1.1)\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_\mathrm{f}H^\circ_\mathrm{m}[\mathrm{CH(CH_3)Cl_2, g}] = -(127.7 \pm 1.4)\ \mathrm{kJ{\cdot}mol^{-1}}$ in ref 5. Note that in their recent review Kerr and Stocker (ref 8), give $DH^\circ(\mathrm{Cl{-}CH_2Cl}) = 350.2 \pm 0.8\ \mathrm{kJ{\cdot}mol^{-1}}$, a considerably different value from that selected in the present paper. This is probably a typo since according to these authors the value was taken from Tschuikow-Roux, E.; Paddison, S. *Int. J. Chem. Kinet.*, **1987**, *19*, 15, who in fact recommend $DH^\circ(\mathrm{Cl{-}CH_2Cl}) = 338.5 \pm 4.2\ \mathrm{kJ{\cdot}mol^{-1}}$. $DH^\circ(\mathrm{Cl{-}CHCH_2}) = 400.0 \pm 5.3\ \mathrm{kJ{\cdot}mol^{-1}}$ was derived from $\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{CH{=}CH_2, g}) = 299.6 \pm 3.3\ \mathrm{kJ{\cdot}mol^{-1}}$ in ref 7 and $\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{ClCH{=}CH_2, g}) = 20.9 \pm 4.2\ \mathrm{kJ{\cdot}mol^{-1}}$ recommended in Colegrove, B. T.; Thompson, T. B. *J. Chem. Phys.* **1997**, *106*, 1480.

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

(59) $DH^\circ[\mathrm{HOOC(CH_3)HC{-}CH(CH_3)COOH}] = 279.1 \pm 6.7\ \mathrm{kJ{\cdot}mol^{-1}}$ is based on the enthalpy of formation of the $CH(CH_3)COOH$ radical obtained in this work and on $\Delta_\mathrm{f}H^\circ_\mathrm{m}[\mathrm{HOOC(CH_3)HC{-}CH(CH_3)COOH, cr}] = -(987.8 \pm 1.4)\ \mathrm{kJ{\cdot}mol^{-1}}$ in ref 5 and on $\Delta_\mathrm{sub}H^\circ_\mathrm{m}[\mathrm{HOOC(CH_3)HC{-}CH(CH_3)COOH}] = 122.7 \pm 2.7\ \mathrm{kJ{\cdot}mol^{-1}}$ reported in Ribeiro da Silva, M. A. V.; Monte, M. J. S.; Ribeiro, J. R. *J. Chem. Thermodynamics* **2001**, *33*, 23. $DH^\circ(\mathrm{ClCH_2{-}CH_2Cl}) = 364.6 \pm 5.3\ \mathrm{kJ{\cdot}mol^{-1}}$ is based on $\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{CH_2Cl, g}) = 119.1 \pm 2.4\ \mathrm{kJ{\cdot}mol^{-1}}$ in ref 57 and on $\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{ClCH_2{-}CH_2Cl, g}) = -(126.4 \pm 2.3)\ \mathrm{kJ{\cdot}mol^{-1}}$ in ref 5.

(60) (a) Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 34. (b) Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 223. The group electronegativity values in Table 4 were directly taken from these references or calculated in this work by the method described therein.