

Energetics of the C–Cl Bond in CH₃CH(Cl)COOH. Enthalpy of Formation of (S)-(-)-2-Chloropropionic Acid and of the 1-Carboxyethyl Radical^{†,‡}

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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 $\Delta_f H_m^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl}, \text{l}) = -(534.6 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1}$, by rotating-bomb combustion calorimetry. The corresponding enthalpy of vaporization, $\Delta_{\text{vap}} H_m^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl}) = (64.9 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$, was also obtained from vapor pressure versus temperature measurements by the transpiration method, leading to $\Delta_f H_m^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl}, \text{g}) = -(469.7 \pm 1.2) \text{ kJ}\cdot\text{mol}^{-1}$. This value, together with the enthalpy of the isodesmic and isogyric gas-phase reaction $\text{CH}_3\text{CH}(\text{X})\text{COOH}(\text{g}) + \text{C}_2\text{H}_5(\text{g}) \rightarrow \text{CH}_3\text{CHCOOH}(\text{g}) + \text{C}_2\text{H}_5\text{X}(\text{g})$ ($\text{X} = \text{H}, \text{Cl}$) 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 $\Delta_f H_m^\circ[\text{CH}(\text{CH}_3)\text{COOH}, \text{g}] = -(293 \pm 3) \text{ kJ}\cdot\text{mol}^{-1}$, from which $DH^\circ[\text{H}-\text{CH}(\text{CH}_3)\text{COOH}] = 380.7 \pm 3.9 \text{ kJ}\cdot\text{mol}^{-1}$ and $DH^\circ[\text{Cl}-\text{CH}(\text{CH}_3)\text{COOH}] = 298.0 \pm 3.2 \text{ kJ}\cdot\text{mol}^{-1}$ 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 , $\text{XCH}(\text{CH}_3)\text{Cl}$, $\text{XCH}=\text{CH}_2$, and XC_6H_5 ($\text{X} = \text{H}, \text{Cl}$). The order $DH^\circ(\text{C}-\text{H}) > DH^\circ(\text{C}-\text{Cl})$ is observed for the carboxylic acids and all other RX compounds. Comparison of $DH^\circ[\text{X}-\text{CH}(\text{CH}_3)\text{COOH}]$ and $DH^\circ[\text{X}-\text{CH}_2\text{COOH}]$ ($\text{X} = \text{H}, \text{Cl}$) 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

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(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 ¹H and ¹³C NMR spectra were obtained at ambient temperature on a Bruker AMX (400 MHz) spectrometer. The ¹³C spectra were recorded at 75.5 MHz. Chemical shifts relative to tetramethylsilane (TMS) were calculated with CHCl₃ 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 cm³ 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 cm³ diethyl ether portions. The ethereal extract was dried over CaCl₂ 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): $\alpha_D^{25} = -17.48^\circ$ (lit. = -18.2° ¹²). IR (NaCl): $\tilde{\nu}/\text{cm}^{-1} = 2993, 2933$ (C–H), 1729 (COO[–]), 1445, 1420 (COO[–], C–H), 1383, 1289, 1256, 1212, 1076, 990, 921, 858. ¹H NMR (400 MHz, CDCl₃/TMS): $\delta = 1.73$ (d, *J* = 7.12 Hz, 3 H, CH₃), $\delta = 4.46$ (q, *J* = 7.12, 1 H, CH). ¹³C NMR (75.5 MHz, CDCl₃/TMS): $\delta = 21.40$ (s, CH₃), $\delta = 52.41$ (s, CH), $\delta = 176.36$ (s, COO). Elemental analysis for C₃H₅O₂Cl: 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 $T_{\text{fus}} = (266.2 \pm 1.2)$ K. The corresponding enthalpy of fusion was $\Delta_{\text{fus}}H_m^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl}) = (9.8 \pm 0.3)$ kJ·mol^{–1}. The uncertainties quoted for both values represent twice the standard deviation of the mean of five independent determinations.

Heat Capacity Measurements 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 -Al₂O₃ 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, $T_{\text{fus}} = 243.75$ K; *n*-octadecane, $T_{\text{fus}} =$

301.47 K; hexatriacontane, $T_{\text{fus}} = 347.30$ K; indium, $T_{\text{fus}} = 430.61$ K; and tin, $T_{\text{fus}} = 506.03$ 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 cm³·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 cm³·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*-C₁₁H₂₄ 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 cm³·s^{–1} was used as the carrier gas in the analysis. At the end of each transpiration run, 200 μ L of a standard solution of *n*-C₁₁H₂₄ in CH₃CN of concentration 4.65 g·dm^{–3} was added to the trap containing the condensed (S)-(–)-2-chloropropionic acid, and 0.1 μ L of the resulting mixture was injected in the GC apparatus. The corresponding mass of sample (*m*) was then obtained from $m/m_{\text{st}} = a + b(A/A_{\text{st}})$, where $m_{\text{st}} = 0.93$ mg is the mass of *n*-C₁₁H₂₄, *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*-C₁₁H₂₄.

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 $0.11 \text{ cm}^3\cdot\text{s}^{-1} \leq q_v \leq 1.5 \text{ cm}^3\cdot\text{s}^{-1}$ was selected. In the present experiments, flow rates of 0.946 or 0.960 cm³·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 dm³, 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 cm³ of a 0.09016 mol·dm⁻³ As₂O₃(aq) was placed inside the bomb. The presence of the arsenious oxide solution ensured that all Cl₂ 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 μ F 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 HNO₃ formed from traces of atmospheric N₂ remaining inside the bomb was analyzed by the Devarda's alloy method.²¹ The extent of the reaction of Cl₂ formed in the combustion with the arsenious oxide solution was found by titrating the final bomb solution with sodium thiosulfate (0.100 mol·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 method²³ with the Perdew and Wang PW91²⁴ 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 from²⁶

$$E = V_{\text{NN}} + H^{\text{CORE}} + V_{\text{ee}} + E_{\text{X}}[\rho] + E_{\text{C}}[\rho] \quad (1)$$

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 $E_{\text{X}}[\rho]$ and $E_{\text{C}}[\rho]$ 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-pVDZ²⁹ 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-pVTZ³⁰ 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

<i>m</i> /mg	<i>V</i> _{N₂} /dm ³	<i>T</i> /K	<i>p</i> /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 $C_{\text{p,m}}^{\circ}(\text{C}_3\text{H}_5\text{O}_2\text{Cl}, \text{l}) = (260 \pm 6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, where the uncertainty quoted represents twice the standard deviation of the mean of three independent results. This value is in agreement with $C_{\text{p,m}}^{\circ}(\text{C}_3\text{H}_5\text{O}_2\text{Cl}, \text{l}) = (252 \pm 25) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ 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 $C_{\text{p,m}}^{\circ}(\text{C}_3\text{H}_5\text{O}_2\text{Cl}, \text{l}) = 149$ and $209 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively.³² These lower predictions probably reflect the inadequacy of the method to estimate $C_{\text{p,m}}^{\circ}$ 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 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. The average of these two values, $C_{\text{p,m}}^{\circ}(\text{C}_3\text{H}_5\text{O}_2\text{Cl}, \text{g}) = 101.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, 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

$$p = \frac{mRT_{\text{a}}}{MV_{\text{N}_2}} \quad (2)$$

where $R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is the gas constant, *M* is the molar mass of the sample, $T_{\text{a}} = 296 \pm 1 \text{ K}$ is the ambient temperature, and V_{N_2} is the total volume of N₂ used as carrier gas throughout the experiment. The obtained results were fitted to the Clausius–Clapeyron equation

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

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 N₂ 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

$m(\text{C}_3\text{H}_5\text{O}_2\text{Cl})/\text{g}$	0.751 36	0.744 81	0.853 54	0.840 12	0.769 25	0.792 62	0.790 81
$m(\text{cotton})/\text{g}$	0.002 69	0.002 28	0.002 81	0.002 65	0.002 70	0.002 69	0.002 47
$m(n\text{-C}_{16}\text{H}_{34})/\text{g}$	0.302 26	0.299 59	0.295 15	0.303 57	0.302 17	0.294 68	0.301 97
$m(\text{Melinex})/\text{g}$	0.044 94	0.042 06	0.045 09	0.044 59	0.041 13	0.050 03	0.045 58
$\Delta m(\text{H}_2\text{O})/\text{g}$	1.7	0.8	1.5	1.3	-0.5	0.1	0.1
$10^5 \times n(\text{HNO}_3)/\text{mol}$	8.0	5.0	3.0	4.0	8.0	10.0	5.0
$10^4 \times n(\text{As}_2\text{O}_3)/\text{mol}$	5.02	4.09	4.69	4.75	4.09	4.36	4.12
$10^6 \times n(\text{H}_2\text{PtCl}_6)/\text{mol}$	2.08	2.12	3.18	1.67	2.52	2.24	1.59
$\epsilon_i/\text{J}\cdot\text{K}^{-1}$	94.95	94.93	95.11	95.10	94.97	95.01	95.01
$\epsilon_f/\text{J}\cdot\text{K}^{-1}$	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
$\Delta T_c/\text{K}$	0.017 60	0.017 27	0.017 44	0.017 48	0.017 16	0.016 88	0.017 20
$\Delta U_{\text{ign}}/\text{J}$	1.29	1.29	1.29	1.29	1.29	1.29	1.29
$-\Delta U_{\text{IBP}}/\text{J}$	25 112.41	24 799.00	26 098.11	26 301.23	25 232.66	25 393.15	25 583.72
$\Delta U_{\Sigma}/\text{J}$	46.03	35.50	48.02	48.27	46.25	46.80	47.05
$\Delta U(\text{HNO}_3)/\text{J}$	4.78	2.98	1.79	2.39	4.78	5.97	2.98
$\Delta U(\text{As}_2\text{O}_3)/\text{J}$	160.68	130.93	150.12	152.36	130.93	139.56	131.88
$\Delta U(\text{H}_2\text{PtCl}_6)/\text{J}$	0.51	0.52	0.78	0.41	0.62	0.55	0.39
$\Delta U(\text{Melinex})/\text{J}$	1029.16	963.36	1032.58	1021.16	941.89	1145.89	1043.78
$-\Delta U(\text{cotton})/\text{J}$	43.69	37.03	45.63	43.04	43.85	43.69	40.11
$-\Delta U(n\text{-C}_{16}\text{H}_{34})/\text{J}$	14 254.39	14 128.32	13 918.68	14 315.78	14 250.14	13 896.96	14 240.70
$\Delta U(\text{C}_3\text{H}_5\text{O}_2\text{Cl})/\text{J}$	9573.17	9500.36	10 900.51	10 717.82	9814.20	10 113.73	10 076.83
$-\Delta_c u^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl})/\text{J}\cdot\text{g}^{-1}$	12 741.12	12 755.41	12 770.94	12 757.49	12 758.14	12 759.87	12 742.42

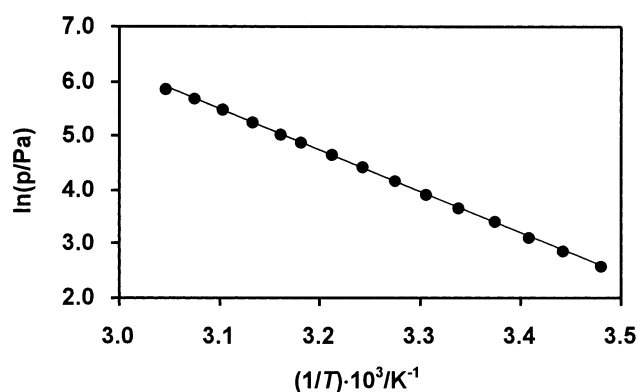


Figure 1. Vapor pressure of (S)-(-)-2-chloropropionic acid as a function of the temperature.

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 $\pm 0.001 \text{ dm}^3$ 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 $b = -\Delta_{\text{vap}}H_m^\circ/R = -(7629.8 \pm 65.7) \text{ K}$ with a regression coefficient of 0.9999. The corresponding plot of $\ln p$ versus $1/T$ is presented in Figure 1. From these results, $\Delta_{\text{vap}}H_m^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl}) = 63.4 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$ at the mean temperature of the temperature range covered by the experiments, $T_m = 307.9 \text{ K}$, is obtained. The uncertainties quoted for a and b and $\Delta_{\text{vap}}H_m^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl})$ 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:

$$\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K}) = \Delta_{\text{vap}}H_m^\circ(307.9 \text{ K}) + \Delta_{\text{vap}}C_{p,m}^\circ(298.15 \text{ K} - 307.9 \text{ K}) \quad (4)$$

where $\Delta_{\text{vap}}C_{p,m}^\circ$ represents the difference in heat capacity of the gaseous and liquid compound. This leads to $\Delta_{\text{vap}}H_m^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl}) = 64.9 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$ at 298.15 K.

The results of the combustion calorimetric experiments are shown in Table 2, where $m(\text{C}_3\text{H}_5\text{O}_2\text{Cl})$ is the mass of (S)-(-)-2-chloropropionic acid; $m(\text{cotton})$ represents the mass of the cotton thread fuse of empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$; $m(\text{Melinex})$ is the mass of the Melinex bag containing the sample; $m(n\text{-C}_{16}\text{H}_{34})$ is the mass of n -hexadecane used as combustion auxiliary; $\Delta m(\text{H}_2\text{O})$ 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); $n(\text{HNO}_3)$ is the amount of substance of nitric acid formed in the bomb process; $n(\text{As}_2\text{O}_3)$ is the amount of substance of arsenious oxide consumed in the reaction with the Cl_2 ; $n(\text{H}_2\text{PtCl}_6)$ 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); $\Delta U(\text{HNO}_3)$ is the energy change associated with the formation of nitric acid; $\Delta U(\text{As}_2\text{O}_3)$, 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; $\Delta U(\text{H}_2\text{PtCl}_6)$ represents the energy change associated with the conversion of Pt to H_2PtCl_6 , in the bomb process; $\Delta U(\text{Melinex})$, $\Delta U(\text{cotton})$, $\Delta U(n\text{-C}_{16}\text{H}_{34})$, and $\Delta U(\text{C}_3\text{H}_5\text{O}_2\text{Cl})$ 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, $\Delta_c u^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl})$ 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(CH₃)COOH(g) at 298.15 K^a

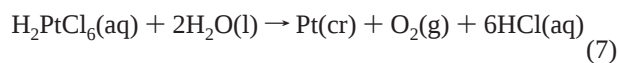
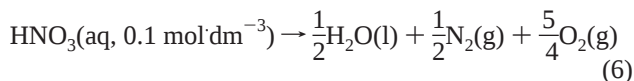
method	X = H		X = Cl	
	−Δ _r H _m (11)	−Δ _r H _m [CH(CH ₃)COOH, g]	−Δ _r H _m (11)	−Δ _r H _m [CH(CH ₃)COOH, g]
B3PW91/6-31G(d,p)	40.7	293.6	56.5	295.1
B3PW91/6-311+G(d,p)	37.5	290.4	54.4	293.0
B3PW91/aug-cc-pVDZ	36.7	289.6	54.7	293.3
B3PW91/aug-cc-pVTZ//	38.0	290.9	55.5	294.1
B3PW91/aug-cc-pVDZ				

^a Data are given in kilojoules per mole.

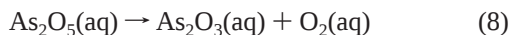
T_i , T_f , and ΔT_c were calculated by using a computer program³⁵ based on the Regnault-Pfaundler method,^{36–38} and ΔU_{IBP} was derived from³⁹

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

The energy equivalent of the calorimeter and its standard deviation, $\epsilon_o = 25177.4 \pm 1.4 \text{ J}\cdot\text{K}^{-1}$, 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 $-(26432.3 \pm 3.8) \text{ J}\cdot\text{g}^{-1}$. 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, $c_p^\circ = 2.215 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$,⁴⁴ $\rho = 0.773 \text{ g}\cdot\text{cm}^{-3}$,⁴⁴ and $-(\partial u/\partial p)_T = 0.347 \text{ J}\cdot\text{MPa}^{-1}\cdot\text{g}^{-1}$,⁴⁵ for (S)-(−)-2-chloropropionic acid, $c_p^\circ = 2.396 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ (this work, see above), $\rho = 1.2585 \text{ g}\cdot\text{cm}^{-3}$,⁴⁴ $-(\partial u/\partial p)_T = 0.20 \text{ J}\cdot\text{MPa}^{-1}\cdot\text{g}^{-1}$.⁴⁶ The values of $\Delta U(\text{HNO}_3)$ and $\Delta U(\text{H}_2\text{PtCl}_6)$ correspond to the processes



and were obtained from the following data: $\Delta_f U_m^\circ(\text{HNO}_3, \text{aq}, 0.1 \text{ mol}\cdot\text{dm}^{-3}) = -59.7 \text{ kJ}\cdot\text{mol}^{-1}$ ⁴⁷ and $\Delta_r U_m^\circ(7) = 245.6 \text{ kJ}\cdot\text{mol}^{-1}$.⁴⁸ The term $\Delta U(\text{As}_2\text{O}_3)$, corresponds to

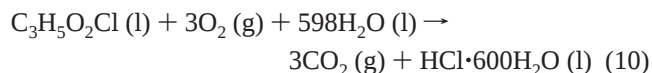


It depends on the concentration of As_2O_5 and H^+ in the final bomb solution and was derived for each experiment by using the equations and data given by Hu et al.⁴² The calculation of $\Delta U(\text{cotton})$, and $\Delta U(\text{Melinex})$ was based on $\Delta_c u^\circ(\text{cotton}) = -16250 \text{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

$$\Delta_c u^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl}) = [\Delta U_{IBP} + \Delta U_\Sigma + \Delta U(\text{HNO}_3) + \Delta U(\text{As}_2\text{O}_3) + \Delta U(\text{H}_2\text{PtCl}_6) - \Delta U(\text{cotton}) - \Delta U(n\text{-C}_{16}\text{H}_{34}) - \Delta U(\text{Melinex})]/m(\text{C}_3\text{H}_5\text{O}_2\text{Cl}) \quad (9)$$

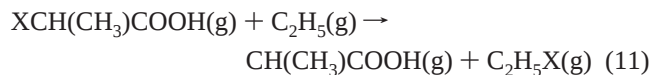
The mean value of the standard massic energies of combustion of (S)-(−)-2-chloropropionic acid indicated in Table 2 is $\Delta_c u^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl}) = -(12755.06 \pm 3.92) \text{ J}\cdot\text{g}^{-1}$, where the

uncertainty quoted is the standard deviation of the mean. This result refers to



and leads to $\Delta_c U_m^\circ = \Delta_c H_m^\circ = -(1384.22 \pm 1.04) \text{ kJ}\cdot\text{mol}^{-1}$. 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 $\Delta_c H_m^\circ$ value indicated above and $\Delta_f H_m^\circ(\text{CO}_2, \text{g}) = -(393.51 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$,⁵³ $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) = -(285.830 \pm 0.040) \text{ kJ}\cdot\text{mol}^{-1}$,⁵³ and $\Delta_f H_m^\circ(\text{HCl}\cdot 600\text{H}_2\text{O}, \text{l}) = -(166.619) \text{ kJ}\cdot\text{mol}^{-1}$,⁴⁷ it is possible to derive $\Delta_f H_m^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl}, \text{l}) = -(534.6 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1}$. This value differs by $10.9 \text{ kJ}\cdot\text{mol}^{-1}$ from $\Delta_f H_m^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl}, \text{l}) = -(523.7 \pm 8.3) \text{ kJ}\cdot\text{mol}^{-1}$,^{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 $\Delta_f H_m^\circ(\text{C}_3\text{H}_5\text{O}_2\text{Cl}, \text{g}) = -(469.7 \pm 1.2) \text{ kJ}\cdot\text{mol}^{-1}$.

The standard enthalpy of formation of the CH(CH₃)COOH radical was derived from the enthalpy of the isodesmic and isogyric reaction 11, $\Delta_r H_m^\circ(11)$, calculated by DFT for X = H, Cl (Table 3). The $\Delta_f H_m^\circ[\text{CH}(\text{CH}_3)\text{COOH}, \text{g}]$ values in Table 3 were obtained through eq 12 by using the enthalpy of formation of gaseous ClCH(CH₃)COOH determined in this work ($-469.7 \pm 1.2 \text{ kJ}\cdot\text{mol}^{-1}$) and $\Delta_f H_m^\circ(\text{CH}_3\text{CH}_2\text{COOH}, \text{g}) = -(455.7 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$,⁵ $\Delta_f H_m^\circ(\text{C}_2\text{H}_6, \text{g}) = -(83.8 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}$,⁵ $\Delta_f H_m^\circ(\text{C}_2\text{H}_5\text{Cl}, \text{g}) = -(112.1 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1}$,⁵ and $\Delta_f H_m^\circ(\text{C}_2\text{H}_5, \text{g}) = 119 \pm 2 \text{ kJ}\cdot\text{mol}^{-1}$.⁵⁶



$$\Delta_f H_m^\circ[\text{CH}(\text{CH}_3)\text{COOH}, \text{g}] = \Delta_f H_m^\circ(11) - \Delta_f H_m^\circ(\text{C}_2\text{H}_5\text{X}, \text{g}) + \Delta_f H_m^\circ(\text{C}_2\text{H}_5, \text{g}) + \Delta_f H_m^\circ[\text{XCH}(\text{CH}_3)\text{COOH}, \text{g}] \quad (12)$$

As seen in Table 3, the $\Delta_r H_m^\circ(11)$ results are quite insensitive to the basis set used in the calculation. In addition, the values of $\Delta_f H_m^\circ[\text{CH}(\text{CH}_3)\text{COOH}, \text{g}]$ obtained from the several $\Delta_r H_m^\circ(11)$ 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 $\Delta_f H_m^\circ[\text{CH}(\text{CH}_3)\text{COOH}, \text{g}]$, $-(293 \pm 3) \text{ kJ}\cdot\text{mol}^{-1}$, is the mean of the results in Table 3. This value, together with $\Delta_f H_m^\circ(\text{H}, \text{g}) = 217.998 \pm 0.006 \text{ kJ}\cdot\text{mol}^{-1}$,⁵³ $\Delta_f H_m^\circ(\text{Cl}, \text{g}) = 121.301 \pm 0.008 \text{ kJ}\cdot\text{mol}^{-1}$,⁵³ and

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

R	X		R
	H (2.25)	Cl (3.10)	
CH ₂ COOH (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 ₂ H ₅ (2.32)	420.8 ± 2.0 ^b	352.4 ± 2.3 ^b	363.7 ± 2.9 ^b
CH ₂ Cl (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 ^c	489.2 ± 4.8 ^b
C ₆ H 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 electronegativities⁶⁰ of the R and X fragments are given in parentheses.

^b Reference 3. ^c This work. ^d Reference 59. ^e Reference 57.

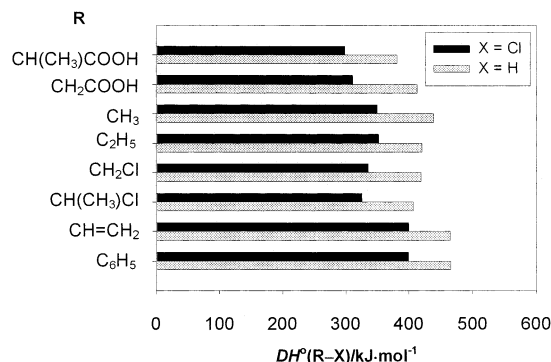


Figure 2. R–H and R–Cl bond dissociation enthalpies.

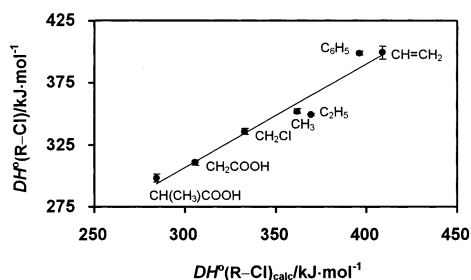


Figure 3. Experimental R–Cl bond dissociation enthalpies, $DH^\circ(\text{R}-\text{Cl})$, from Table 4, versus the corresponding values calculated from eq 13, $DH^\circ(\text{R}-\text{Cl})_{\text{calc}}$, for $\text{R} = \text{CH}_2\text{COOH}$, $\text{CH}(\text{CH}_3)\text{COOH}$, CH_3 , C_2H_5 , CH_2Cl , $\text{CH}(\text{CH}_3)\text{Cl}$, $\text{CH}=\text{CH}_2$, and C_6H_5 .

the standard enthalpies of formation of $\Delta_f H_m^\circ[\text{XCH}(\text{CH}_3)\text{COOH}, \text{g}]$ ($\text{X} = \text{H}, \text{Cl}$) indicated above, yield the bond dissociation enthalpies $DH^\circ[\text{H}-\text{CH}(\text{CH}_3)\text{COOH}] = 380.7 \pm 3.9 \text{ kJ}\cdot\text{mol}^{-1}$ and $DH^\circ[\text{Cl}-\text{CH}(\text{CH}_3)\text{COOH}] = 298.0 \pm 3.2 \text{ kJ}\cdot\text{mol}^{-1}$. 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 , $\text{XCH}(\text{CH}_3)\text{Cl}$, $\text{XCH}=\text{CH}_2$, and XC_6H_5 ($\text{X} = \text{H}, \text{Cl}$) quoted or calculated from the literature.^{3,57} The order $DH^\circ(\text{C}-\text{H}) > DH^\circ(\text{C}-\text{Cl})$ is observed for the carboxylic acids and all other RX compounds in Table 4 (Figure 2). Comparison of $DH^\circ[\text{X}-\text{CH}(\text{CH}_3)\text{COOH}]$ and $DH^\circ[\text{X}-\text{CH}_2\text{COOH}]$ ($\text{X} = \text{H}, \text{Cl}$) 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 $DH^\circ(\text{C}-\text{H})$,⁸ and $DH^\circ(\text{C}-\text{Cl})$ with the notable exception $DH^\circ(\text{Cl}-\text{CH}_3) \leq DH^\circ(\text{Cl}-\text{C}_2\text{H}_5)$ (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 $DH^\circ(\text{R}-\text{Cl})$ values in Table 4 and the corresponding $DH^\circ(\text{R}-$

$\text{Cl})_{\text{calc}}$ values calculated from Pauling's arithmetic mean expression:

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

where $\chi_{\text{Cl}} = 3.10$ and χ_{R} are the electronegativities of Cl and R, respectively, by using $DH^\circ(\text{Cl}-\text{Cl}) = 242.602 \pm 0.011 \text{ kJ}\cdot\text{mol}^{-1}$ and the $DH^\circ(\text{R}-\text{R})$,^{3,59} and group electronegativity⁶⁰ data given in Table 4, respectively. This correlation corresponds to

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

with a regression coefficient of 0.98. The average error in the estimation of $DH^\circ(\text{R}-\text{Cl})$ from eq 14 is $8.8 \text{ kJ}\cdot\text{mol}^{-1}$.

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 ($\text{R} = \text{H}, \text{CH}_3$)⁹



From the enthalpy of formation of gaseous 2-chloropropionic acid determined in this work ($-469.7 \pm 1.2 \text{ kJ}\cdot\text{mol}^{-1}$), $\Delta_f H_m^\circ(\text{ClCH}_2\text{COOH}, \text{g}) = -(427.55 \pm 1.04) \text{ kJ}\cdot\text{mol}^{-1}$,³ $\Delta_f H_m^\circ(\text{CO}, \text{g}) = -(110.52 \pm 0.17) \text{ kJ}\cdot\text{mol}^{-1}$,⁵³ $\Delta_f H_m^\circ(\text{HCl}, \text{g}) = -(92.31 \pm 0.10) \text{ kJ}\cdot\text{mol}^{-1}$,⁵³ $\Delta_f H_m^\circ(\text{HCHO}, \text{g}) = -(108.6 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$,⁵ and $\Delta_f H_m^\circ(\text{CH}_3\text{CHO}, \text{g}) = -(166.1 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$,⁵ it is possible to conclude that $\Delta_r H_m^\circ(15) = 116.1 \pm 1.3 \text{ kJ}\cdot\text{mol}^{-1}$ ($\text{R} = \text{H}$) and $100.8 \pm 1.3 \text{ kJ}\cdot\text{mol}^{-1}$ ($\text{R} = \text{CH}_3$). 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: $80.42 \text{ kJ}\cdot\text{mol}^{-1}$ (MP2/6-31G**), 82.80 (MP2/6-31++G**), and $65.53 \text{ kJ}\cdot\text{mol}^{-1}$ (CISD/6-31G**) with a scale factor of 0.91, or $77.64 \text{ kJ}\cdot\text{mol}^{-1}$ (MP2/6-31G**), 80.03 (MP2/6-31++G**), and $62.61 \text{ kJ}\cdot\text{mol}^{-1}$ (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 $\Delta_r H_m^\circ(15)$ value by $18\text{--}38 \text{ kJ}\cdot\text{mol}^{-1}$.

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