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# Enthalpies of combustion and formation of 2-acetylpyrrole, 2-acetylfuran and 2-acetylthiophene

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ABSTRACT

The combustion energies for 2-acetylpyrrole (cr) and 2-acetylfuran (cr) were determined using a static bomb calorimeter, whereas the combustion energy of 2-acetylthiophene (l) was determined with a rotating bomb calorimeter; both calorimeters have been recently described. The molar combustion energies obtained were: $-(3196.1 \pm 0.6)\,\mathrm{kJ\,mol^{-1}}$ for 2-acetylpyrrole, $-(2933.8 \pm 0.7)\,\mathrm{kJ\,mol^{-1}}$ for 2-acetylfuran, and $-(3690.4 \pm 0.8)\,\mathrm{kJ\,mol^{-1}}$ for 2-acetylthiophene. From these combustion energy values, the standard molar enthalpies of formation in the condensate phase were obtained as: $-(163.51 \pm 0.97)\,\mathrm{kJ\,mol^{-1}}$, $-(283.50 \pm 1.06)\,\mathrm{kJ\,mol^{-1}}$ and $-(123.93 \pm 1.15)\,\mathrm{kJ\,mol^{-1}}$, respectively. The obtained values of combustion and formation enthalpies of 2-acetylthiophene are in concordance with the reported previously. For the two last compounds, polyethene bags were used as an auxiliary material in the combustion experiments. The heat capacities and purities of the compounds were determined using a differential scanning calorimeter.

## 1. Introduction

2-Acetylpyrrole (2ACP), 2-acetylfuran (2ACF), and 2-acetylthiophene (2ACT) are derivatives from five-carbon aromatic heterocyclic compounds, with an acetyl group on position 2 and a different heteroatom (N, O, or S) in position 1 which confers different properties to each compound.

It is well known that the responsible compounds of aroma in many commercial products are some aromatic heterocycles found in nature. It has been found, for example, that 2ACP is a compound responsible of typical popcorn aroma characteristics [1] and of the cooked rice aroma [2], and it was also found in brewed coffee [3,4]. The reaction of 2ACP with nitrite produces 1-nitro-2-acetylpyrrole, which is markedly cytotoxic to mouse C3H10T1/2 cells. This suggests that the formation of direct-acting mutagens may take place in foods containing nitrites as preservatives [5]. 2ACF is a compound responsible of tomato paste and mango aroma [6,7]. 2ACP and 2ACF were found in fruit juices concentrates [8] and as Maillard products from the thermal decomposition of glucose-1-phosphate [9]. 2ACF, as part of CBS-1108 (2-acetylthiophene 2-thiazolylhydrazone), inhibits the activities of 5-lipoxygenase in polymorphonuclear leukocytes, and of 12-lipoxygenase and cyclooxygenase in platelets [10].

On other hand, the reactivity on photooxidation of 2ACP, 2ACF, and 2ACT, with singlet oxygen has been studied using a high performance liquid chromatographic method [11].

In spite of their uses and applications, no measured values of combustion energies and formation enthalpies for 2ACP and 2ACF were found in the literature. For 2ACT, the combustion and formation enthalpies are reported by Roux et al. as $-(3702.5 \pm 1.6)\,\mathrm{kJ\,mol^{-1}}$ and $-(118.0 \pm 1.7)\,\mathrm{kJ\,mol^{-1}}$, respectively [12].

The aim of the present work is to report the experimental determination of the standard combustion energies and formation enthalpies in condensate phase of 2ACP, 2ACF, and 2ACT at $T = 298.15\,\mathrm{K}$ using two different calorimetric systems; a static-bomb calorimeter and a rotating-bomb calorimeter. Fig. 1 shows the molecular structures of the studied compounds.

2ACP, 2ACF, and 2ACT are derivatives of pyrrole, furan, and thiophene, respectively. Formation enthalpies in liquid phase, $\Delta_f H_m^{\circ}(\mathrm{l})$, were determined some years ago, as $(63.1 \pm 0.4)\,\mathrm{kJ\,mol^{-1}}$ for pyrrole [13], $-(62.3 \pm 0.7)\,\mathrm{kJ\,mol^{-1}}$ for furan [14], and $(80.96 \pm 0.63)\,\mathrm{kJ\,mol^{-1}}$ [15] for thiophene.

## 2. Experimental

The 2ACP, 2ACF, and 2ACT were supplied by Sigma–Aldrich Co. with a fraction mass of 0.999 and were used without additional purification. The purities, molar heat capacities, fusion temperatures and fusion enthalpies of these compounds were determined

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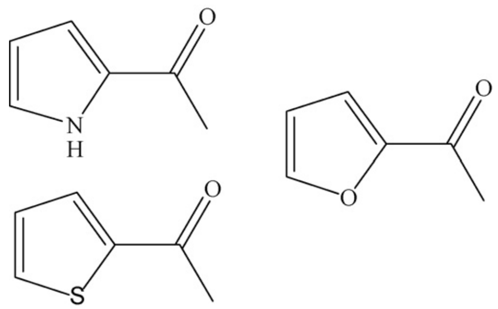

**Fig. 1.** Molecular structures of 2-acetylpyrrole (2ACP), 2-acethylfuran (2ACF) and 2-acetylthiophene (2ACT).

with a TA Instrument 2010 differential scanning calorimeter (DSC).

The calibration constant and the thermal resistance for the temperature correction of the DSC were obtained by the fusion of high-purity indium [16]. The purities, temperatures and enthalpies of fusion were determined from fusion peak analysis using the fractional fusion technique, with non-hermetic aluminum cells under a constant flow of dry gaseous nitrogen, and performing the respective corrections for thermal lag and undetermined premelting [17].

The molar heat capacities were obtained by the three steps method using synthetic sapphire as reference over a (263.15–333.15) K temperature range [18–20].

Table 1 shows the parameters determined by differential scanning calorimetry and the auxiliary quantities used in the calculation of the combustion energies of the compounds.

The combustion experiments for 2ACP and 2ACF were carried out in an isoperibolic static bomb calorimeter, which has a Parr 1108 static bomb, with an internal volume of 0.345 $dm^3$. The calorimeter has been recently described and its equivalent value in energy is $\varepsilon(\text{calor}) = (10149.69 \pm 0.34)\,J\,K^{-1}$ [25]. The static combustion bomb was placed inside the calorimeter vessel, which contained 2000.0 g of distilled water.

The 2ACP and 2ACF samples, in pellets, were burnt in a platinum crucible (mass of approximately 11.55 g) in the presence of 0.001 $dm^3$ of demineralized water and 2.53 MPa (for 2ACP) and 2.03 MPa (for 2ACF) of high-purity oxygen (Air Liquide Corp., mass fraction of 0.99999). The combustion experiments for 2ACP and 2ACF were carried out at the mentioned pressures, due to a tendency of the compounds to spill out of the crucible at higher pressures. To remove atmospheric nitrogen from the bomb, the bomb was flushed by letting oxygen pass through for 5 min. After this flushing time, the outlet valve bomb is closed and the oxygen inside attains the final pressure. To obtain complete combustion in the 2ACF combustion experiments, polyethene bags were used as an auxiliary material with a specific combustion energy $\Delta_c u^\circ = -(46.3726 \pm 0.0022)\,kJ\,g^{-1}$ and the empirical formula $C_1H_{2.073}$ [25].

The combustion experiments of 2ACT were carried out in a rotating-bomb calorimeter with a platinum lining Parr 1004 combustion bomb with an internal volume of 0.348 $dm^3$. This calorimeter has been recently described and its equivalent value is $\varepsilon(\text{calor}) = (14321.2 \pm 2.4)\,J\,K^{-1}$ [26]. The combustion bomb was placed inside the calorimeter vessel, which contained 2700.0 g of distilled water.

The 2ACT was burnt, using polyethene bags to contain the liquid samples, in a platinum crucible of 6.41 g of mass, in the presence of 0.01 $dm^3$ of demineralized water and under 2.53 MPa of oxygen inside the bomb, without flushing to foster the formation of sulphuric acid in the final state of the bomb.

The aqueous phase resultant in the bomb after the combustion process was quantitatively transferred to a flask, and together with the bomb rinsing water, was diluted to a 0.1 $dm^3$ volume. Aliquots of 0.01 $dm^3$ were taken from the solution and titrated with a standard sodium hydroxide solution (0.1 mol $dm^{-3}$). The nitric acid quantity was taken as the difference between the total acidity and the sulphuric acid quantity calculated from the mass of the sample [24,27]. Also, the nitric acid quantity was determined using Devarda's alloy method and no energetically significant difference was found.

In both, the rotating-bomb and the static-bomb calorimeters, the energy needed to start the combustion process inside the bomb was supplied by a Parr 2901 ignition unity. The circuit was closed with a platinum wire connected to the sample by a cotton thread with specific energy $\Delta_c u^\circ = -(16.9452 \pm 0.0042)\,kJ\,g^{-1}$ and the empirical formula $C_1H_{1.742}O_{0.921}$ [23,28].

The apparent mass of all the substances and materials involved in the combustion process were measured with an ME215S Sartorius balance (accuracy of ±0.01 mg) and corrections to mass were applied.

The temperature rise in each combustion experiment was measured with a 5610 Hard Scientific thermistor calibrated over the temperature range of (273.15–373.15) K. The resistances were measured with an HP 34420 A digital multimeter connected to a PC to obtain automatic recording of data. The values of resistance were converted to temperature values through a calibration equation.

The corrected temperature rise, the correction of apparent mass to mass, and the Washburn corrections were obtained by means of computer programs developed in our laboratory on the basis of reports found in literature [29–31].

## 3. Results and discussion

The results for the combustion energies were obtained from 8 experimental runs for 2ACP, 8 for 2ACF, and 7 for 2ACT. Table 2 shows typical combustion experiments for each compound corresponding, respectively, to the following reactions:

$$C_6H_7ON(s) + 7.25O_2(g) = 6CO_2(g) + 3.5H_2O(l) + 0.5N_2(g) \quad (1)$$

$$C_6H_6O_2(s) + 6.5O_2(g) = 6CO_2(g) + 3H_2O(l) \quad (2)$$

$$\begin{aligned} &C_6H_6OS(l) + 8.5O_2(g) + 113H_2O(l) \\ &\quad = 6CO_2(g) + (H_2SO_4{\cdot}115\,H_2O)(aq) \quad (3) \end{aligned}$$

**Table 1**
Physical properties of compounds and materials which took part in the combustion process at $T = 298.15$ K.

| | $M^a$ ($g\,mol^{-1}$) | $\rho$ ($g\,cm^{-3}$) | $-(\partial u/\partial p)_T$ ($J\,g^{-1}\,MPa^{-1}$) | $C_p$ ($J\,g^{-1}\,K^{-1}$) | $\Delta_{fus}H^b$ ($kJ\,mol^{-1}$) | $T_{fus}$ $(K)^b$ |
|---|---|---|---|---|---|---|
| 2ACP | 109.119 | 1.224 [22] | 0.2 | $1.21 \pm 0.03^b$ | 14.08 ± 0.52 | 362.97 ± 0.02 |
| 2ACF | 110.105 | 1.098 | 0.2 | $1.28 \pm 0.03^b$ | 15.51 ± 0.30 | 301.62 ± 0.06 |
| 2ACT | 126.171 | 1.171 | 0.2 | $1.67 \pm 0.04^b$ | | |
| Polyethene | 14.100 | 0.938 [24] | 0.228 [24] | 2.0 [24] | | |
| Cotton | 28.502 | 1.500 [23] | 0.289 [23] | 1.647 [23] | | |

Estimated values as in ref. [23].

[a] Molecular masses are based on 2005 IUPAC recommendations [21].

[b] Experimental values.

**Table 2**
Typical results of combustion experiments of 2ACP, 2ACF and 2ACT at $T = 298.15$ K and $p^\circ = 0.1$ MPa.

| | 2ACP | 2ACF | 2ACT |
|---|---|---|---|
| $m'$ (cpd.) (g) | 0.90033 | 0.86010 | 0.85212 |
| $m''$ (polyethene) (g) | 0.00000 | 0.08872 | 0.07136 |
| $m'''$ (cotton) (g) | 0.00205 | 0.00318 | 0.00305 |
| $m$ (platinum) (g) | 11.52364 | 11.52787 | 6.41779 |
| $T_i$ (K) | 295.2873 | 295.2999 | 296.1042 |
| $T_f$ (K) | 297.9301 | 298.0137 | 298.0901 |
| $\Delta T_c = (T_f - T_i + \Delta T_{corr})$ (K) | 2.6003 | 2.6663 | 1.9729 |
| $\varepsilon_i$ (cont.) (kJ K$^{-1}$) | 0.0155 | 0.0141 | 0.0527 |
| $\varepsilon_f$ (cont.) (kJ K$^{-1}$) | 0.0166 | 0.0152 | 0.0530 |
| $\Delta U_{ign}$ (kJ) | 0.0042 | 0.0042 | 0.0042 |
| $-\Delta U_{IBP}$ (kJ) | 26.4282 | 27.0950 | 28.3531 |
| $\Delta U_{dec}$ ($HNO_3$) (kJ) | 0.0081 | 0.0000 | 0.0456 |
| $n$ ($HNO_3$) | 0.0001 | | 0.0008 |
| $\Delta U_\Sigma$ (kJ) | 0.0138 | 0.0126 | 0.0231 |
| $-m''\Delta_c u^\circ$ (polyethene) (kJ) | 0.0000 | 4.1140 | 3.3090 |
| $-m'''\Delta_c u^\circ$ (cotton) (kJ) | 0.0347 | 0.0539 | 0.0517 |
| $-\Delta_c u^\circ$ (kJ g$^{-1}$) | 29.2910 | 26.6417 | 29.2490 |

$m'$ (cpd.), mass of compound; $m''$ (polyethene), mass of polyethene; $m'''$ (cotton), mass of the cotton thread; $m$ (platinum), mass of platinum which includes crucible and wire for ignition; $\Delta T_c$, corrected temperature rise; $\varepsilon$ (cont.), energy equivalent of the bomb contents; $\Delta U_{ign}$, ignition energy; $\Delta U_{IBP}$, energy of the isothermal bomb process; $\Delta U_{dec}$ ($HNO_3$); energy of decomposition of the nitric acid; $n$ ($HNO_3$) quantity of nitric acid in moles; $\Delta U_\Sigma$, correction to standard state, which include the energy of dilution of the sulphuric acid (for 2ACT); $\Delta_c u^\circ$ (cpd.), massic energy of combustion.

**Table 3**
Individual values for combustion experiments of 2ACP, 2ACF and 2ACT at $T = 298.15$ K and $p^\circ = 0.1$ MPa.

| 2ACP | 2ACF | 2ACT |
|---|---|---|
| $-\Delta_c u^\circ$ (kJ g$^{-1}$) | | |
| 29.2990 | 26.6417 | 29.2608 |
| 29.3097 | 26.6408 | 29.2530 |
| 29.2812 | 26.6677 | 29.2601 |
| 29.2958 | 26.6683 | 29.2414 |
| 29.2750 | 26.6494 | 29.2603 |
| 29.2864 | 26.6221 | 29.2490 |
| 29.2910 | 26.6417 | 29.2434 |
| 29.2816 | 26.6330 | 29.2410 |
| | | 29.2402 |
| | | 29.2426 |
| $\langle -\Delta_c u^\circ \rangle$ (kJ g$^{-1}$) | | |
| 29.2900 ± 0.0040 | 26.6456 ± 0.0056 | 29.2492 ± 0.0027 |

Table 3 shows the individual values of each combustion experimental run for 2ACP, 2ACF, and 2ACT. The corrections for nitric acid were based on the value of $-0.59$ kJ mol$^{-1}$ for the molar energy of formation of 0.1 mol dm$^{-3}$ of $HNO_3$(aq) solution from $O_2$(g), $N_2$(g) and $H_2O$(l) [32]. The formation enthalpy of $H_2SO_4 \cdot 115H_2O$(aq), for the formation enthalpy calculus for 2ACT, was taken as $-(887.811 \pm 0.011)$ kJ mol$^{-1}$ [33].

The values of the standard molar energy $\Delta_c U_m^\circ$(cr,l) and enthalpy $\Delta_c H_m^\circ$(cr,l) of combustion, and the standard molar enthalpy of formation $\Delta_f H_m^\circ$(cr,l) of the compounds studied here are shown in Table 4.

The standard molar enthalpies of formation of $H_2O$(l) and $CO_2$(g) at $T = 298.15$ K are $-(285.830 \pm 0.0042)$ kJ mol$^{-1}$ and $-(393.51 \pm 0.13)$ kJ mol$^{-1}$, respectively. They were taken from CODATA [33]. The uncertainties in the standard molar energy and enthalpy of combustion are the final overall standard deviation of the mean and were estimated as outlined by Olofsson [34].

**Table 4**
Standard molar energy and enthalpy of combustion and the standard molar enthalpy of formation of the compounds at $T = 298.15$ K and $p^\circ = 0.1$ MPa.

| | $-\Delta_c U_m^\circ$ (kJ mol$^{-1}$) | $-\Delta_c H_m^\circ$ (kJ mol$^{-1}$) | $-\Delta_f H_m^\circ$ (kJ mol$^{-1}$) |
|---|---|---|---|
| 2ACP(cr) | 3196.1 ± 0.6 | 3197.9 ± 0.6 | 163.51 ± 0.97 |
| 2ACF(cr) | 2933.8 ± 0.7 | 2935.0 ± 0.7 | 283.50 ± 1.06 |
| 2ACT(l) | 3690.4 ± 0.8 | 3696.6 ± 0.8 | 123.93 ± 1.15 |

Detailed results of all the experimental combustion experiments are presented in Tables A–C (in a supplementary data file).

The formation enthalpies of 2ACP, 2ACF and 2ACT in the condensate phase increase as the heteroatom electronegativity decreases. This behavior has been observed in other series of compounds such as in benzimidazole, benzothiazole, and benzoxazole [35,36], in 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and 2-mercaptobenzoxazole [27], and in pyrrole, furan, and thiophene [13–15].

From formation enthalpies analysis, it observes an average decrement of $(219.28 \pm 7.78)$ kJ mol$^{-1}$ when pyrrole, furan and thiophene are substituted in the 2 position by an acetyl group to produce 2ACP, 2ACF and 2ACT. The last fact suggests that position 2 is energetically equivalent in the three heterocyclic compounds.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2009.04.012.

## References

[1] D. Park, J.A. Maga, Food Chem. 99 (2006) 538–545.
[2] R.G. Buttery, J.G. Turnbaugh, L.C. Ling, J. Agric. Food Chem. 36 (1988) 1006–1009.
[3] M.D. Fuster, A.E. Mitchell, H. Ochi, T. Shibamoto, J. Agric. Food Chem. 48 (2000) 5600–5603.
[4] K. Yanagimoto, K.G. Lee, H. Ochi, T. Shibamoto, J. Agric. Food Chem. 50 (2002) 5480–5484.
[5] C.J. Wang, Y.L. Lin, J.K. Lin, Food Chem. Toxicol. 32 (1994) 839–844.
[6] R.G. Buttery, R. Teranishi, L.C. Ling, J.G. Turnbaugh, J. Agric. Food Chem. 38 (1990) 336–340.
[7] M. Sakho, J. Crouzet, S. Seck, J. Food Sci. 50 (1985) 548–550.
[8] J.P. Yuan, F. Cheng, J. Agric. Food Chem. 46 (1998) 1286–1291.
[9] V.A. Yaylayan, D. Michiels, L. Istasse, J. Agric. Food Chem. 51 (2003) 3358–3366.
[10] C. Bertez, M. Miouel, C. Coquelet, D. Sincholle, C. Bonne, Biochem. Pharmacol. 33 (1984) 1757–1762.
[11] C.W. Chen, C.T. Ho, J. Agric. Food Chem. 44 (1996) 2078–2080.
[12] M.V. Roux, M. Temprado, P. Jiménez, R. Notario, J.S. Chickos, A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Phys. Chem. A 111 (2007) 11084–11092.
[13] D.W. Scott, W.T. Berg, I.A. Hossenlopp, W.N. Hubbard, J.F. Messerly, S.S. Todd, D.R. Douslin, J.P. McCullough, G. Waddington, J. Phys. Chem. 71 (1967) 2263–2270.
[14] G.B. Guthrie, D.W. Scott, W.N. Hubbard, C. Katz, J.P. McCullough, M.E. Gross, K.D. Williamson, G. Waddington, J. Am. Chem. Soc. 74 (1952) 4662–4669.
[15] S. Sunner, Acta Chem. Scand. 17 (1963) 728–730.
[16] W.Wm. Wendlandt, Thermal Analysis, 3rd ed., Willey, New York, 1986.
[17] G.W.H. Höhne, W.F. Hemminger, H.-J. Flammersheim, Differential Scanning Calorimetry, 2nd ed., Springer-Verlag, New York, 2003.
[18] M.J. O'Neill, Anal. Chem. 38 (1966) 1331–1336.
[19] L. Chiu, H. Liu, M. Li, J. Chem. Eng. Data 44 (1999) 631–636.
[20] L. Becker, O. Aufderhaar, J. Gmehling, J. Chem. Eng. Data 45 (2000) 661–665.
[21] M.E. Weiser, Pure Appl. Chem. 78 (2006) 2051–2066.
[22] E.A. Camarillo, H. Flores, P. Amador, S. Bernès, Acta Crys. E 63 (2007) 2593–2594.
[23] W.D. Good, N.K. Smith, J. Chem. Eng. Data 14 (1969) 102–106.
[24] M.V. Roux, J.Z. Dávalos, P. Jiménez, H. Flores, J.-L. Saiz, J.L.-M. Abboud, J. Chem. Thermodyn. 31 (1999) 635–646.
[25] H. Flores, P. Amador, J. Chem. Thermodyn. 36 (2004) 1019–1024.
[26] H. Flores, J. Mentado, P. Amador, L.A. Torres, M. Campos, A. Rojas, J. Chem. Thermodyn. 38 (2006) 756–759.
[27] J. Mentado, H. Flores, P. Amador, J. Chem. Thermodyn. 40 (2008) 1106–1109.
[28] S.P. Verevkin, J. Chem. Thermodyn. 30 (1998) 1069–1079.
[29] W.N. Hubbard, D.W. Scott, G. Waddington, in: F.D. Rossini (Ed.), Experimental Thermochemistry, Interscience, New York, 1956.
[30] W.D. Good, J.L. Lacina, J.P. Mc Collough, J. Am. Chem. Soc. 82 (1960) 5589–5591.
[31] I. Wadsö, Sci. Tools 13 (1966) 33–39.

[32] The NBS tables of chemical thermodynamic properties, J. Phys. Chem. Ref. Data 11 (Suppl. 2) (1982).
[33] J.D. Cox, D.D. Wagman, V.A. Medvedev (Eds.), CODATA Key Values for Thermodynamics, Hemisphere, New York, 1987.
[34] G. Olofosson, in: M. Sunner, Mansson (Eds.), Combustion Calorimetry, Pergamon Press, Oxford, 1979 (Chapter 6).
[35] P. Jiménez, M.V. Roux, C. Turrion, F. Gomis, J. Chem. Thermodyn. 19 (1987) 985–992.
[36] W.V. Steele, R.D. Chirico, S.E. Knipmeyer, A. Nguyen, J. Chem. Thermodyn. 24 (1992) 499–529.