ESTIMATION OF THE THERMODYNAMIC PROPERTIES OF SEVERAL OXYGENATED COMPOUNDS INVOLVED IN BIOMASSES PYROLYSIS

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As already well established, the products of biomasses pyrolysis can be important in the exploration of alternatives to the use of fossil fuels. The study of the kinetic mechanism of thermal degradation of biomasses requires the knowledge of thermodynamic properties of the species, molecules and radicals, involved in the reaction path. These properties have been estimated by using the group contributions method and the program THERM. Particularly in the case of radicals the use of THERM can be difficult and, asan alternative, here is proposed a criterion based onanalogy rules(isodesmicmethod). The obtained properties have been tabulated and compared with the experimental data where available. Moreover a comparison among the methods has been performed. A useful databank for several oxygenated compounds involved in biomasses pyrolysis has been obtained.

1. INTRODUCTION

In a continuously pressing research for higher performance, increased selectivity and faster development of new processes, accurate models describing both pyrolysis and combustion of biomasses are required. As well known these processes are based on complex reaction systems involving radicals and hundreds of kinetically significant reaction intermediates. The development of a detailed kinetic model based on elementary reactions is, therefore, challenging. Our research group, beside others (Susnowet al., 1997, De Witt et al., 2000, Green et al., 2001), has a long history in this field (Dente et al., 1979, Dente et al., 2007, Calonaci et al., 2010). The development of these kinetic schemes requires the estimation of kinetic and thermodynamic parameters. Through the equilibrium constant of a reaction it is possible to deduce the direct or reverse kinetic constant once one of the two in known (for instance available on NIST or deduced by means of analogy rules with other similar reactions). It is therefore essential to have an appropriate tool for the estimation of thermodynamic properties. Despite the increasing computational power, the *ab-initio* calculation of kinetic and thermodynamic parameters for all the components (for instance by using G3MP2B3), is not realistic,even if it seems to give reliable results when compared with experimental data. The reasons are mainly three (Saeys et al., 2004). First, the number of involved reactions would require the evaluation of too many kinetic and thermodynamic parameters. Second, the discrepancy between experimental data and *ab-initio* calculation increases with the size of analyzed molecule or radical. Last, but not least, it is too much time consuming. Other methods of estimation, alternative to *ab-initio* calculations, are substantially based on the additivity of the properties of themolecule constituting groups. In the present work three methods have been considered. First Benson's group contributions method (1960) has been adopted. Then calculations have been performed by using the THERM program (Ritter and Bozzelli, 1991).Finally, in the case of radicals, where the evaluation of properties can be, in general, more difficult, a specific method is proposed. It is based on a concept similar to isodesmic calculations (Zhu and Bozzelli, 2003). The calculated properties have been compared, finally, with the experimental ones, where available (e.g. Handbook of Chemistry and Physics, referred as HB, and Burcat and Ruscic database).For free radicals and other short-livedintermediates, direct calorimetric measurements arenot possible, while spectroscopic investigationsrequire quite skill and sophisticated instrumentation. Consequently, for a number of free radicals, thermochemical data are still uncertain.

2. CRITERIA APPLIED INTO THE METHOD

Any group contributions method consists, of course, in the subdivision of the molecule in constituent groups, each of them contributing to the required property. In practice, by defining as Y this property, it is simply evaluated by an addition rule:

$$Y = \sum_{i=1}^{GN} n_i B_i \qquad (1)$$

where B_i is the contributions of group "i" on the total number of groups GN, and n_i is the group occurrence inside the molecule. A sufficiently complete database for group contributions evaluation has been given in a pioneering work by Benson (1960). This method can be also applied to radicals, however the database in this case is lacking of information. Benson (1960) reported only some more diffused radical groups. For the characterization of the radical properties, and mainly for the enthalpy of formation, it is not sufficient to evaluate just the contribution of the group containing the unpaired electron, but it is also necessary evaluating how the adjacent groups are influenced by the presence of the radical position. Therefore it is clear that the number of group contributions necessary is larger than that usually available in the literature. Consequently it isconvenient to find a way for solving the problem. A first solution seems to be to use the program THERM (Ritter and Bozzelli, 1991). It allows evaluating the thermodynamic properties ($\Delta H°$, $S°$, Cp) of molecules and radicals and it is based on the use of group contributions method. Moreover entropy calculation requires the evaluation of the symmetrynumber; this can be difficult for large molecules or radicals. The database of THERM contains also that of Benson but, for radical properties evaluation, it is more extended. In some caseseven THERM doesn't contain a specific group, but a method similar to isodesmic calculations can be used. It can be applied only for the evaluation of ΔH_f. It consists in using the group contributions method for evaluating the ΔH_f of the hydrogenatedparent molecule. Then the properties of the radical are deduced by adding a contribution obtained by analogy with a similar, but generally wellknown, molecule and the corresponding, dehydrogenated, radical.

Fig. 1: structure of (C₅H₃O₂) and (C₄H₅O₃) radicals

In order to better clarify the procedure, the following two examples are reported. In figure 1 are depicted the two radicals considered for the properties evaluation.

Table 1: Calculation of the$\Delta H_f$of $C_5H_4O_2$ molecule

$C_5H_4O_2$Groups	H_f kcal/mole (300°C)
Cd(Cd)(H) x 2	6.78 x 2
Cd(O)(H)	8.6
Cd(O)(CO)	11.6
O(Cd₂)	-33.0
CO(Cd)(H)	-29.1
C_5 cycle	-5.8
Sum ($C_5H_4O_2$)	-34.14

Table 2: Calculation of the ΔH_f of $C_4H_6O_3$ molecule

$C_4H_6O_3$ Groups	H_f kcal/mole (300°C)
CO(O)(Cd)	-32.0
O(CO)(H)	-58.1
Cd(CO)(H)	5.0
Cd(H)(C)	8.59
C(Cd)(O)(H$_2$)	-6.5
O(H)(C)	-37.9
Sum ($C_4H_6O_3$)	-120.91

Radical $C_5H_3O_2$:

ARC: ΔH_f (CH$_2$=CHC•O) – ΔH_f (CH$_2$=CHCHO) = 21.2 + 17.8 = 39 kcal/mol

ΔH_f ($C_5H_3O_2$) = ΔH_f ($C_5H_4O_2$) + ARC = -34.14 + 39 = 4.86 kcal/mol

Radical $C_4H_5O_3$:

ARC: ΔH_f (CH$_3$CH$_2$O•) – ΔH_f (CH$_3$CH$_2$OH) =- 3.25 + 56.09 = 52.84 kcal/mol

ΔH_f ($C_4H_5O_3$) = ΔH_f ($C_4H_6O_3$) + ARC = -120,91 + 52,84 = -68,07 kcal/mol

The adopted method for the deduction of ARC (Analogy Radical Contribution) takes into account the kind of H that is subtracted and the atoms and bonds that are in the neighboring of the radical position. For instance the contribution of an H atoms of a carboxylic acid differs from that of an alcoholic group, because of the presence of the -(CO)- in α position, causing partial shift of the electronic charge towards the terminal hydroxyl.

2.1 Specific rules adopted for the enthalpy of formation of radicals

The adopted rules for enthalpy prediction can bebriefly described as follows. They have been always based on the analogy with similar elementary structures (radicals and molecules with H attached to the same radical position), for which the properties are already well established in the literature (e.g. on HB or NIST web database). In particular the ARC has been deduced for alcoholic (RCOH), acid(RCOOH) and acil (RCHO) hydrogen taking into consideration the contributions describedin table3. The average deduced values are reported at the end of the table. The other kinds of hydrogen in a group near an oxygen containing group (as for instance the H of methyl group in CH$_3$CHO) can be deduced by the analogous H in a hydrocarbon structure by subtracting an average value of about 2 kcal/mole.

Table 3: ARCcontribution (kcal/mole) for H in ROH, RCOOH and RCHO (rad = radical, mol. = molecule)

Alcohols		Acids		Aldeydes	
H_f Rad.- H_f Mol.	ARC	H_fRad.- H_fMol.	ARC	H_f Rad.- H_f Mol.	ARC
CH$_3$O•-CH$_3$OH	52.5	HCOO•-HCOOH	59.5	•CHO-CH$_2$O	37.9
C$_2$H$_5$O•-C$_2$H$_5$OH	52.8	CH$_3$COO•-CH$_3$COOH	60.8	CH$_3$C•O-CH$_3$CHO	38.4±0.4
iC$_3$H$_7$O•-iC$_3$H$_7$OH	54.5±2	C$_6$H$_5$COO•-C$_6$H$_5$COOH	59.8	C$_2$H$_5$C•O-C$_2$H$_5$CHO	37.4
tC$_4$H$_9$O•-tC$_4$H$_9$OH	52.4			(CH$_3$)$_2$CHC•O-(CH$_3$)$_2$CHCHO	36.3
nC$_4$H$_9$O•-nC$_4$H$_9$OH	51			C$_6$H$_5$C•O-C$_6$H$_5$CHO	36.6±0.7
sC$_4$H$_9$O•-sC$_4$H$_9$OH	53.4			(CH$_3$)$_2$CH$_2$C•O-(CH$_3$)$_3$CH$_2$CHO	37.6
(Cd)$_2$-CH$_2$O•-(Cd)$_2$CH$_2$OH	50.35			CdCCH$_3$C•O-CdCH$_3$CHO	39.4±3.5
average	**52.5±1**		**60**		**37.6±2**

Table 4: comparison between experimental data (Hand Book, HB) and THERM (kcal/mole)

	ΔH_f (298K) HB	ΔH_f (298K) THERM	Deviation
$C_2H_5^\bullet$	28.38	29.00	0.62
$C_6H_5^\bullet$	78.86	79.82	0.96
$C_6H_5CH_2C^\bullet H_2$	56.38	56.15	-0.23
$CH_3CH^\bullet OH$	-12.90	-11.60	1.3
$^\bullet CH_2CH_2OH$	-7.41	-7.00	0.41
$CH_3CH_2C^\bullet O$	-7.57	-7.40	0.17
$CH_3(CO)CH_2^\bullet$	-8.12	-9.26	-1.14
$C_6H_5(CO)OCH_2^\bullet$	-16.70	-20.50	-3.8
$C_2H_5O^\bullet$	-4.04	-4.04	0.
$C_6H_5O^\bullet$	11.59	12.10	0.51
$C_6H_5CH_2O^\bullet$	32.49	29.31	-3.18
$CH_3(CO)O^\bullet$	-42.98	-43.38	-0.4

So, for the subtraction of a primary H in a hydrocarbon the ARC is 45.7kcal/mole (deduced for instance from the difference $\bullet CH_2CH_2CH_3$-C_3H_8), while the analogous difference for a primary H near an oxygen containing group is about 43.7 kcal/mole. The same applies to secondary H for which the contribution passes from 43.2 kcal/mole to about 41 kcal/mole (deduced for instance from the difference $CH_3\bullet CH_2CH_3$-C_3H_8)., and for tertiary H where ARC becomes about 39 kcal/mole starting from a value of 41 kcal/mole in the analogous hydrocarbon structure. A particular attention has to be devoted when a resonance is present: in the case of phenoxy resonance a value of 17 has to be subtracted for alcoholic H, so that ARC is 52.5-17≈35. The same happens for $(CdH)_2OH$ having a corresponding radical characterised by resonance.

3. COMPARISONS OF THE RESULTS OBTAINED WITH THE THREE METHODS

The experimental data regarding molecules and radicals are mainly related to ΔH_f (ΔS_f and specific heat are less frequently available). The analogy method can be particularly convenient for evaluating the ΔH_f. Therefore the following comparisons will regard only the enthalpy of formation. Table4 reports a first comparison between experimental $\Delta H_f$and the ones calculated by using THERM. This talbe is useful for emphasizing the validity of the THERM program. For other radicals, when experimental data are not available, a comparison among the three methods is reported (Table 4).Taking into consideration Table 5, it is possible to observe that the ARC method can be considered reliable; as a matter of fact it has the same level of accuracy of Benson and THERM methods also in the case of radical properties evaluation.

Table 5: enthalpy of formation of radicals with different methods: ΔH_f (298K) [kcal/mole]

	ARC	Benson GC	THERM
$[C_4H_3O]C^\bullet O$	1.24	1.17	0.76
$CH_3CH_2O^\bullet$	-4.03	-4.1	-4.04
$CH_2^\bullet CH(OH)_2$	-53.52	-56.28	-52.8
$HOCH_2CH_2O^\bullet$	-39.84	-40.6	-40.04
$CH_3CH_2C^\bullet O$	-7.26	-10.5	-7.4
$CH_2^\bullet (CO)CH_2$	-43.77	-41.58	-43.58
$CH_3(CO)CH_2O^\bullet$	-35.44	-35.5	-33.92
$OH(C_dH)_2CH_2C^\bullet O$	-19.3	-21.08	-23.28
$O^\bullet CH_2(CdH)_2CHO$	-7.75	-8.56	-8.89

Table6:deviations of THERM and GC with respect to ARC method [kcal/mole]

	ARC	GC	THERM	GC-ARC(%)	THERM-ARC (%)
$[C_4H_3O]C^{\bullet}O$	1.24	1.17	0.76	-0.07	-0.48
$CH_3CH_2O^{\bullet}$	-4.03	-4.1	-4.04	-0.07	-0.01
$CH_2^{\bullet}CH(OH)_2$	-53.52	-56.28	-52.8	-2.76	0.72
$HOCH_2CH_2O^{\bullet}$	-39.84	-40.6	-40.04	-0.76	-0.2
$CH_3CH_2C^{\bullet}O$	-7.26	-10.5	-7.4	-3.24	-0.14
$CH_2^{\bullet}(CO)CH_2OH$	-43.77	-41.58	-43.58	2.19	0.19
$CH_3COCH_2O^{\bullet}$	-35.44	-35.5	-33.92	-0.06	1.52
$OH(CdH)_2CH_2C^{\bullet}O$	-19.3	-21.08	-23.28	-1.78	-3.98
$O^{\bullet}CH_2(CdH)_2CHO$	-7.75	-8.56	-8.89	-0.81	-1.14
AVERAGE				-0.44	-0.06

Table6 shows the deviation of Benson GC method and THERMwith regard to ARC method. The major differences can be observed with respect to GC method, probably because Benson contributions work better for small radicals and molecules. From the table it is clear that ARC method can be alternative to the use of THERM. In facts, the average deviation has been found to be of -0.44 and-0.06 (in general a difference of ± 2 kcal is acceptable).

Table 7 reports a large number of radicals which properties result by applying the proposed method. The entropy and enthalpy of formation of the radicals have been calculated. Into the table (*) refers to THERM, figures without label refers to ARC method. A large number of radicals and molecules have been considered which usually are not available in thermodynamic data collections. The evaluation of their basic properties is essential for obtaining an extended and detailed kinetic scheme for biomasses pyrolysis simulation. Of course the method has been applied also to molecules but here, for lacking of space, only radical properties are reported being more difficult to be found into the literature. The obtained results are satisfactory.

Table 7: results obtained with THERM PROGRAM (*) and ARCmethod

Structure	Formula and name	$\Delta H_f(298)$ [kcal/mole)	$S_f(298)$ [cal/mole/K)
	CH_3O_2 dihydroxymethyl	-45 -44.9*	72 72*
	CH_3O_2 (hydroxymethyl) oxidanyl	-39 -39.07*	70 66.1*
	C_2HO_2 oxoacetyl	-14	70
	$C_2H_3O_2$ carboxymethyl	-55 -54*	71.5 72.*
	$C_2H_3O_2$ hydroxyacetyl	-38.3 -36.6*	72.8 74.7*
	$C_2H_3O_2$ 1-hydroxy-2-oxoethyl	-27.8 -28.7*	76 78.21*
	$C_2H_3O_2$ (2-oxoethyl)oxidanyl	-21.5	73

Table 7: continue

Structure	Formula and name	$\Delta H_f(298)$ [kcal/mole)	$S_f(298)$ [cal/mole/K)
	$C_2H_3O_2$ acetyloxidanyl	-43 -43.4*	65.4 66.6*
	$C_2H_3O_2$ [(E)-2-hydroxy ethenyl]oxidanyl	-34.3 -35.8*	72.8 69.5*
	$C_2H_3O_3$ (1-hydroxy-2-oxoethyl)oxidanyl	-69.2 -68.9*	81 79.5*
	C_2H_5O 1-hydroxyethyl	-12.9 -11.6*	67.5 67.9*
	$C_2H_5O_2$ (1-hydroxyethyl) oxidanyl	-50.2 -49.8*	75.1 72.7*
	$C_2H_5O_2$ 2,2-dihydroxyethyl	-55.8	77.5
	$C_2H_5O_2$ 1,1-dihydroxyethyl	-58.5 -57.4*	76. 79.4*
	$C_2H_5O_2$ (1-hydroxyethyl) oxidanyl	-50.3 -49.8*	75.1 72.7*
	$C_2H_5O_2$ 2,2-dihydroxyethyl	-54.7	77.4
	$C_2H_5O_2$ (2-hydroxyethyl) oxidanyl	-40	74.5
	$C_2H_5O_3$ (1,2-dihydroxyethyl) oxidanyl	-86.1 -85.8*	84.6 83.5*
	$C_3H_3O_3$ 2-hydroxy-1,3-dioxopropan-2-yl	-57.8 -58.4*	88 92.3*
	$C_3H_3O_3$ (1,3-dioxopropan-2-yl)oxidanyl	-51.4 -50.8*	86 85.6*
	$C_3H_3O_3$ [(1E)-2-hydroxy-3-oxoprop-1-en-1-yl]oxidanyl	-45.9 -47.9*	84.4 81.7*

Table 7: continue

Structure	Formula and name	$\Delta H_f(298)$ [kcal/mole)	$S_f(298)$ [cal/mole/K)
	C_3H_5O 2-methoxyethenyl	31.5 33.6*	72.7 73.1*
	C_3H_5O propanoyl	-10.3	73.9
	C_3H_5O prop-1-en-2-yloxidanyl	10.5 13.2*	72.4 71.2*
	$C_3H_5O_2$ 3-hydroxy-2-oxopropyl	-41.5	88
	$C_3H_5O_2$ 1-hydroxy-2-oxopropyl	-43 -41.5*	85.6 82.8*
	$C_3H_5O_2$ (1-oxopropan-2-yl) oxidanyl	-32.4	83.4
	$C_3H_5O_2$ (2-oxopropyl)oxidanyl	-35.6	83
	C_3H_7O 1-methoxyethyl	-5.1	79.3
	C_3H_7O 2-hydroxypropyl	-19.5	79.8
	C_3H_7O 1-methoxyethyl	-6.6 -4.95*	79.3 79.9*
	C_3H_7O ethoxymethyl	-2.3 -3.4*	79.5 79.9*
	C_3H_7O 2-hydroxypropan-2-yl	-22.9 -20.7*	78.9 79.8*
	C_3H_7O propan-2-yloxidanyl	-13	76.7
	$C_3H_7O_2$ 2-hydroxy-2-methoxyethyl	-52	89.5
	$C_3H_7O_2$ 2,2-dihydroxypropyl	-68.8	89
	$C_3H_7O_2$ 1-hydroxy-1-methoxyethyl	-52.0 -52.7*	86.4 87.1*

Table7: continue

Structure	Formula and name	$\Delta H_f(298)$ [kcal/mole)	$S_f(298)$ [cal/mole/K]
	$C_3H_7O_2$ (1-hydroxyethoxy) methyl	-52	89.5
	$C_3H_7O_2$ (2-hydroxypropan-2-yl)oxidanyl	-62.6	79.2
	$C_3H_7O_2$ (1-hydroxypropan-2-yl) oxidanyl	-49.3	85.2
	$C_3H_7O_3$ (1,2-dihydroxypropan-2-yl)oxidanyl	-98.6	90.1
	C_4H_3O furan-2-yl	46.4	66.5
	$C_4H_3O_2$ 5-oxo-2,5-dihydrofuran-2-yl	-22.4 -19.0*	75.6 76.9*
	$C_4H_5O_2$ 2-hydroxy-2,5-dihydrofuran-2-yl	-21.4 -19.5*	79.8 81.8*
	$C_4H_5O_2$ 2-hydroxy-2,5-dihydrofuran-2-yl	-18 -16.3*	90 91.0*
	$C_4H_5O_2$ (2E)-4-hydroxybut-2-enoyl	-24.5 -25.7*	90 87.7*
	$C_4H_5O_2$ 2,5-dihydrofuran-2-yloxidanyl	-15	77.4
	$C_4H_5O_2$ [(2E)-4-oxobut-2-en-1-yl]oxidanyl	-8 -8.9*	88.3 86.7*
	$C_4H_5O_2$ but-3-enoyloxidanyl	-22 -22.2*	84 79.7*
	$C_4H_5O_3$ carboxyacetyl	-96.3 -95.8*	93.4 89.8*
	$C_4H_5O_3$ (4-oxobutanoyl) oxidanyl	-72.4 -72.8*	92. 89.4*
	$C_4H_5O_3$ (3-oxobutanoyl) oxidanyl	-73	100.3

Table 7: continue

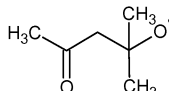| Structure	Formula and name	$\Delta H_f(298)$ [kcal/mole)	$S_f(298)$ [cal/mole/K)
	$C_4H_5O_3$ [(2E)-3-carboxyprop-2-en-1-yl]oxidanyl	-68.9 -69.9*	93.2 91.0*
	$C_4H_5O_3$ 2-ethoxy-2-oxoethyl	-58.9 -59.1*	87.6 86.4*
	$C_4H_7O_2$ 3-hydroxybutanoyl	-51.9 -52.5*	94.4 91.81*
	$C_4H_7O_2$ 1-(2-oxoethoxy)ethyl	-32.9 -33.8*	95.6 94.1*
	$C_4H_7O_2$ 1-(acetyloxy)ethyl	-62 -61.1	88.1 85.5*
	$C_4H_7O_2$ 3-hydroxy-2-oxobutyl	-46.1 -46.4*	95.5 94.1*
	$C_4H_7O_2$ (3-oxobutan-2-yl) oxidanyl	-42.7 -43.4*	90 87.9*
	$C_4H_7O_2$ (4-oxobutan-2-yl) oxidanyl	-37.6 -37.4*	92 89.2*
	C_4H_9O 2-hydroxy-2-methylpropyl	-27.9 -25.5*	85.2 84.6*
	C_4H_9O 2-methoxypropan-2-yl	-17.9 -16.1*	88.9 89.6*
	C_4H_9O 2-methoxypropyl	-17.2 -11.5*	86.7 86.9*
	C_4H_9O (propan-2-yloxy)methyl	-12.4 -16.1*	85.3 83.9*
	C_4H_9O tert-butyloxidanyl	-22.7 -22.5*	77.2 76.2*
	$C_4H_9O_2$ 1-hydroxy-2-methoxypropan-2-yl	-52.8 -52.1*	98 98.1*

Table 7: continue
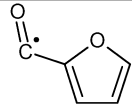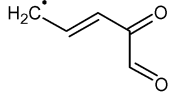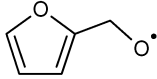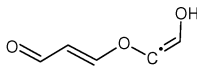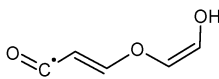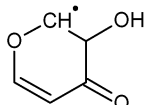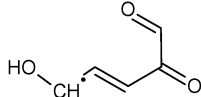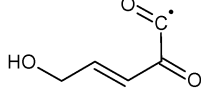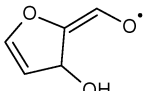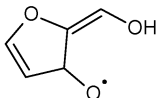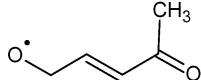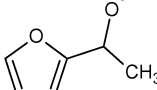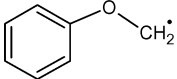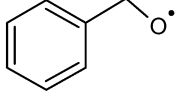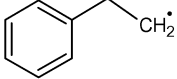
Structure	Formula and name	$\Delta H_f(298)$ [kcal/mole)	$S_f(298)$ [cal/mole/K]
	$C_5H_3O_2$ furan-2-ylcarbonyl	1.9 0.76*	78.4 79*
	$C_5H_5O_2$ (2E)-4,5-dioxopent-2-en-1-yl	-10	96
	$C_5H_5O_2$ (furan-2-ylmethyl) oxidanyl	-0.1 -0.04*	85 84.1*
	$C_5H_5O_3$ (Z)-2-hydroxy-1-{[(1E)-3-oxoprop-1-en-1-yl]oxy}ethenyl	-12.2	106
	$C_5H_5O_3$ (1E)-1-{[(Z)-2-hydroxyethenyl]oxy}-3-oxoprop-1-en-3-yl	-33.2	106
	$C_5H_5O_3$ 3-hydroxy-4-oxo-3,4-dihydro-2H-pyran-2-yl	-53.5 -53.6*	87.5 86.7*
	$C_5H_5O_3$ (2E)-1-hydroxy-4,5-dioxopent-2-en-1-yl	-51.3	104.4
	$C_5H_5O_3$ [furan-2-yl(hydroxy)methyl]oxidanyl	-47.9 -49.3*	104.4 102.3*
	$C_5H_5O_3$ [(E)-(3-hydroxyfuran-2(3H)-ylidene)methyl]oxidanyl	-44.2	93.9
	$C_5H_5O_3$ [(2E)-2-(hydroxymethylidene)-2,3-dihydrofuran-3-yl]oxidanyl	-37.2	93.9
	$C_5H_7O_2$ [(2E)-4-oxopent-2-en-1-yl]oxidanyl	-21 -20.8*	97.5 94.6*
	$C_6H_7O_2$ [1-(furan-2-yl)ethyl]oxidanyl	-7.4 -9.3*	93.8 91.4*
	$C_6H_{11}O_2$ (2-methyl-4-oxopentan-2-yl)oxidanyl	-59.7 -59.2*	107.8 103.1*

Table 7: continue

Structure	Formula and name	$\Delta H_f(298)$ [kcal/mole)	$S_f(298)$ [cal/mole/K]

phenoxymethyl	C_7H_7O	27.8 26.54*	88.2 87.7*
benzyloxidanyl	C_7H_7O	29.4 29.3*	86.8 87.4*
2-phenylethyl	C_8H_9	53.9 56.15*	88.4 92.2*

Also a comparison with the Burcat collection databank (Burcat and Ruscic, 2005) has been performed when possible and the data are in line with those reported into the HB collection. The major part of radicals here reported are not contained in the Burcat collection and a comparison is not possible.

4. DISCUSSION AND CONCLUSIONS

From the reported comparisons and the other analyzed data it can be observed that the more complex structures, containing aromatic rings and multiple bonds, present the higher deviations.Probably, this is due to the fact that the groups are ibridated sp2 producing a stabilizing resonance not taken into account.
The elaboration of a significant number of data related to oxygenated compounds originated ARC contributions for the subtraction of H inROH, RCOOH and RCHOpositions. Also an interesting extra correction for H subtraction in primary, secondary and tertiary position is proposed when oxygen in present in the neighboring group. The ARCcan be used for the evaluationof the enthalpy of formation of more complex radicals offering reliable results, while GC and THERM are more convenient for the entropy and specific heat calculation. This offers a simple tooluseful for the development of large and complex kinetic schemes describing the pyrolysis and combustion of oxygenated species. Finally, it is worth to say that ARC method, because of its simplicity, can be used for quickly verifying the reliability of the results obtained with the other methods. Of Course the properties of the parent molecules are built on the basis of small or large group contribution method.

5. ACKNOWLEDGMENTS

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