Evaluation of the Enthalpy of Formation, Proton Affinity, and Gas-Phase Basicity of γ-Butyrolactone and 2-Pyrrolidinone by Isodesmic Reactions

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The knowledge of thermochemical parameters such as the enthalpy of formation, gas-phase basicity, and proton affinity may be the key to understanding molecular reactivity. The obtention of these thermochemical parameters by theoretical chemical models may be advantageous when experimental measurements are difficult to accomplish. The development of ab initio composite models represents a major advance in the obtention of these thermochemical parameters, but these methods do not always lead to accurate values. Aiming at achieving a comparison between the ab initio models and the hybrid models based on the density functional theory (DFT), we have studied γ-butyrolactone and 2-pyrrolidinone with a goal of obtaining high-quality thermochemical parameters using the composite chemical models G2, G2MP2, MP2, G3, CBS-Q, CBS-4, and CBS-QB3; the DFT methods B3LYP, B3P86, PW91PW91, *m*PW1PW, and B98; and the basis sets 6-31G(d), 6-31+G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d), 6-311+G(d), 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), *aug*-cc-pVDZ, and *aug*-cc-pVTZ. Values obtained for the enthalpies of formation, proton affinity, and gas-phase basicity of the two target molecules were compared to the experimental data reported in the literature. The best results were achieved with the use of DFT models, and the B3LYP method led to the most accurate data.

The obtention of thermochemical parameters in the gas phase is of utmost importance in chemistry because these parameters are related to molecular reactivity and charge reorganization during the ionization process. In many cases, protonation/deprotonation is the main event concerning ion production in the gas phase, and the characteristics of ions and molecules in the absence of solute/solvent interactions allow one to obtain intrinsic parameters related to changes in the electronic structure and acid−base chemistry.[1]

Interpretation of the acidity/basicity of neutral molecules is vital to both the chemical and pharmaceutical industry because the behavior of reaction intermediates will depend on their basicity. Studies concerning proton affinity and basicity in the gas phase may be established for different families and/or group of compounds by means of a scale.[2,3] The effect of the molecular structure on the acid−base behavior of a compound is a very up-to-date topic because the Brönsted quantitative definition of basicity and acidity contributes to the theories of organic compound reactivity.[2]

Various experimental methods, such as calorimetry, kinetic method, and ion cyclotron resonance (ICR), can be used to study these properties.[3,4] The main difficulties encountered with these experimental analyses lie in the physicochemical properties of the investigated molecule, the previous knowledge of the experimental procedures, and the stability of the studied system during the analysis.[4] These difficulties may be overcome by using computational chemistry, where the target thermodynamic properties may be estimated and related to other molecular parameters, like the molecular geometry.[5]

Theoretical models provide information at the atomic level, thus contributing to a better interpretation and refinement of the experimental results.[6] Therefore, it is essential that a comparison between experimental and theoretical models is established and that the limitations of the current theoretical models and their reality in the face of everyday problems are evaluated.

Although computational chemistry can in principle be applied to any system, the errors inherent in thermochemical calculations may lead to significant deviations from experimental values. In an attempt to minimize these errors, isodesmic reactions have been very frequently employed in the obtention of thermochemical parameters of neutral or ionic organic and inorganic molecules.[7−14] Both theoretical and experimental values are usually combined in these hypothetical reactions.[7−9] The most accurate values are those in which the character of the chemical bonds and atom hybridization are maintained for both reagents and products, in the homodesmic reaction.[11,13]

Because it is sometimes difficult to formulate isodesmic reactions, in these cases, the use of quasi-isodesmic reactions and the atomization energies can be made for obtaining themochemical parameters.[14] However, the results obtained by using these two approaches are not very exact when compared to isodesmic/homodesmic reactions.[15,16] Thus, some methods aimed at the obtention of accurate thermochemical parameters have been developed in recent years. Among these methods are basis set extrapolation, multicoefficient methods, and composite chemical models. The complete basis set (CBS),[17] the Gaussian-n models (G*n*),[18] the Weizmann-n (W*n*) method,[19] and the multicoefficient correlation methods (MCCMs) are the ones that furnish the best results.[20] The CBS models use high correlation level methods combined with basis set extrapolation.[17] The W*n* models were designed by Martin and de Oliveira and they are

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similar to the CBS models in that the extrapolation of an infinite basis set is used to estimate the electronic correlation.[17] In contrast, G*n* models[18] often estimate the energy with high correlation level by means of a large basis set. This is done on the basis of high-level calculations for zero-point energy correction.

The main limitation of these methods is their computational cost, which makes their application to larger systems such as natural products virtually impossible. A convenient alternative to the obtention of thermochemical parameters is the use of hybrid functionals based on density functional theory (DFT).[13,14,21,22] The DFT methods are less demanding in terms of computational costs and provide satisfactory results.[7,14−16]

Several works have thoroughly investigated the real ability of different models to predict thermochemical parameters. To this end, Smith and Random tested whether a series of Gaussian models, MP4, and DFT methods were able to reproduce experimental values concerning proton affinity, and they came to the conclusion that the DFT models were the least accurate.[23] On the other hand, Catalan and Palomar investigated the acidity and basicity of a certain number of species employing B3LYP/6-311+G(2df, 3pd), and their results led to an excellent correlation with the experimental data.[24]

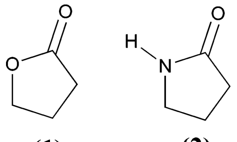
Lactones are cyclic esters that can have a large number of carbon atoms, but researchers' attention has been driven to the small lactone rings because of their high reactivity and difficult obtention.[25] The reactivity of these esters is a significant issue because numerous biological molecules contain lactones in their structures.[26] Lactams belong to a class of cyclic amides that are structurally analogous to lactones but have higher basicity.[26,27] Some lactones and lactams occur naturally, but the synthesis of these compounds has attracted researchers' interest[28] because they can act as antibiotic, antifungal,[29] and analgesic[30] agents, not to mention the fact that they can be used as flavoring agents in the food industry.[31]

The gas-phase basicity (GB) of lactams, ketones, and cyclic amides has already been obtained by FTICR-MS and calculated by MP2/6-31G(d), and the experimental values agreed well with the calculated ones.[32,33] Studies with B3PW1 and B3LYP functionals with 6-31++G(d,p) and *aug*-cc-pVDZ basis sets have been carried out for the possible dimers of 2-pyrrolidinone, and the stability of these molecules in face of intramolecular hydrogen bonds has been investigated.[34] The data indicated that the stability of the dimers is related to structural parameters and intermolecular energetic interactions. In another study, the intrinsic basicity of a series of saturated and unsaturated lactones was calculated using G2(MP2,SVP), where the absolute errors were in the order of 3 kJ mol^{-1}.[35] Except for β-propyolactone, lactones are generally more basic than the corresponding aliphatic esters (same number of carbon atoms), and their basicity increases with increasing ring size.[35]

Several methods such as the composite chemical models, DFT and ab initio calculations have been used to estimate lactone basicity.[34−36] However, the number of works describing a systematic search for their intrinsic thermochemical parameters is still small. Verifying which method is the most suitable for investigating the stability of these molecules and their derivatives and the gas-phase reactivity is therefore crucial.[35−37]

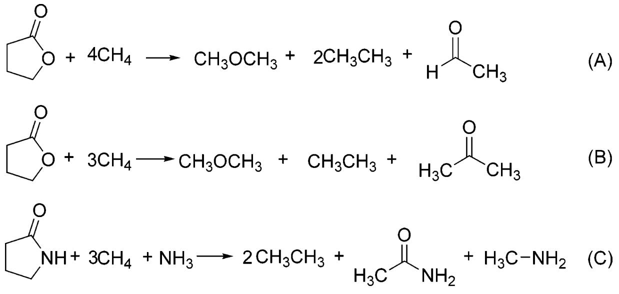
In this work, we have calculated the enthalpy of formation of γ-butyrolactone (**1**) and 2-pyrrolidinone (**2**) (Scheme 1) by means of some isodesmic reactions, employing a series of DFT methods with various Gaussian basis functions, and composite models. Proton affinity and gas-phase basicity were calculated for these molecules, and the theoretical values were compared with the experimental data. Within the framework of a project aiming at studying the fragmentation mechanisms of natural products by ESI-MS, we attempted to gain a better knowledge of the best model for the obtention of thermochemical parameters for this kind of molecules.

SCHEME 1: Structure of (1) δ-Butyrolactone and (2) 2-Pyrrolidinone

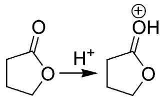


(1) **(2)**

SCHEME 2: Isodesmic Reactions for the Enthalpy of Formation Calculations: (A, B) γ-Butyrolactone; (C) 2-Pyrrolidinone



SCHEME 3: Protonation Site on γ-Butyrolactone



Computational Details

Three isodesmic reactions (Scheme 2) were initially proposed for the obtention of the enthalpy of formation of 2-pyrrolidinone and γ-butyrolactone.

All the molecules involved in the reactions had their most stable conformer optimized by calculation of their vibrational frequencies using GAUSSIAN 98[38] and GAUSSIAN 03 software.[39] The composite chemical models CBS-Q, CBS-4, CBS-QB3,[14] G3, G2, and G2(MP2);[15] methods based on the density functional theory, such as B3LYP,[40,41] PBE1PBE,[42] PW91PW91,[43] mPW1PW91,[44] B3P86,[45] and B98;[46] the set of basis functions 6-31G(d), 6-31+G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G-(d,p), 6-311G(d), 6-311+G(d), 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p),[47,48] *aug*-cc-pVDZ and *aug*-cc-pVTZ;[49] and the MP2 method[50] were employed for the same set of basis function. The reaction enthalpies of the isodesmic reactions were calculated, as well as the enthalpies of formation of 2-pyrrolidinone and γ-butyrolactone.

Proton affinities in the gas phase were estimated from the enthalpy of the following heterolytic reaction: $M + H^+ = MH^+$, where M is the target molecule. The enthalpy of formation and the free energy of the proton were obtained by statistical thermodynamics.[51] As indicated by other studies, the energetically most favorable site of γ-butyrolactone protonation site is the carbonyl oxygen (see Scheme 3).[36,52]

For the protonation reaction, the gas-phase basicity is defined as the negative of the Gibbs energy.[1−4,53] The heat of formation of the proton can be estimated from the ideal gas law, and the proton entropy can be calculated by the Sackur−Tetrode equation.[54]

TABLE 1: Enthalpies of Formation at 298.15 K, in kJ mol^{-1}[a]

compds	$\Delta H_{\text{formation}}$
CH_4	−74.87
$CH_3C(O)NH_2$	−238.33
CH_3NH_2	−22.50
CH_3CH_3	−83.80
2-pyrrolidinone	−197.40
NH_3	−45.90
CH_3OCH_3	−184.10
CH_3CHO	−170.70
γ-butyrolactone	−365.00
$CH_3C(O)CH_3$	−218.50

[a] See Chase, M.W., Jr. *NIST-JANAF Themochemical Tables*, 4th ed.; Journal of Physical and Chemical Reference Data, Monograph 9; American Insitute of Physics: Melville, NY, 1998; pp 1−1951; webbook.nist.gov/chemistry.

TABLE 2: Calculated Enthalpies for Reaction (A) (ΔH_{rx}; Scheme 2), Enthalpy of Formation (ΔH_f), and Respective Errors for γ-Butyrolactone ($\Delta\Delta H_f$ and $\Delta\Delta H_{rx}$; kcal mol^{-1})[a]

model	ΔH_{rx}	$\Delta\Delta H_{rx}$	ΔH_f	$\Delta\Delta H_f$
B3LYP/6-31G(d)	34.17	0.24	−87.90	−0.67
B3LYP/6-31+G(d)	32.80	−1.13	−86.53	0.70
B3LYP/6-31G(d,p)	34.46	0.53	−88.18	−0.95
B3LYP/6-31+G(d,p)	33.46	−0.47	−87.19	0.04
B3LYP/6-31++G(d,p)	33.36	−0.57	−87.09	0.14
B3LYP/6-311G(d,p)	34.66	0.73	87.96	−0.73
B3LYP/6-311+G(d,p)	33.16	−0.53	86.47	−0.76
B3LYP/6-311++G(d,p)	33.12	−0.56	86.43	−0.80
B3P86/6-31G(d)	35.74	1.81	−89.47	−2.24
B3P86/6-31+G(d)	34.35	0.42	−88.08	−0.85
B3P86/6-31G(d,p)	36.08	2.15	−89.81	−2.58
B3P86/6-31+G(d,p)	34.83	0.90	−88.55	−1.32
B3P86/6-31++G(d,p)	34.74	0.81	−88.05	−0.82
G3	36.56	2.63	−89.87	−1.17
G2	36.40	2.47	−90.13	−2.90
G2(MP2)	35.92	1.99	−89.65	−2.42
CBS-Q	36.95	3.02	−90.68	−3.45
MP2/6-31++G(d,p)	35.34	1.41	−88.65	−1.42
B98/6-31+G(d,p)	33.55	−0.37	−86.86	−0.37
B98/6-31++G(d,p)	33.46	−0.47	−86.77	−0.46

[a] ΔH_{rx}(exp) = 33.93 kcal mol^{-1} and ΔH_f(exp)= −87.23 kcal mol^{-1}.[55]

In the standard conditions, the proton gas-phase enthalpy and entropy are $H(H^+) = 1.48$ kcal mol^{-1} and $S(H^+) = 26.01$ cal mol^{-1}, respectively, which gives a gas-phase free energy, $G(H^+)$, of= −6.28 kcal mol^{-1}.[51]

The proton affinities and gas-phase basicity were obtained at 298.15 K and 1 atm using the reaction between the neutral molecule and the proton, which led to the protonated γ-butyrolactone. Our results were compared with the experimental values reported in the literature.[55,56] The models that led to the smallest absolute errors were employed in the calculation of the proton affinity and gas-phase basicity of 2-pyrrolidinone.

The enthalpies of formation were obtained following eq 1. The enthalpy for this reaction, $\Delta H_{\mathbf{rx}\text{calculated}}$, was calculated on the basis of theoretical enthalpies of formation for each compound (Table 1). Using $\Delta H_{\mathbf{rx}\text{calculated}}$ and experimental enthalpy of formation for A, C, and D, the enthalpy of formation for target molecule (M), $\Delta H_{f\mathbf{M}}$, was obtained (eq 2).[57]

$$A + M \rightarrow C + D \tag{1}$$

$$\Delta H_{\mathbf{rx}\text{calculated}} = [\Delta H_{f\mathbf{C}\text{calculated}} + \Delta H_{f\mathbf{D}\text{calculated}}] - [\Delta H_{f\mathbf{A}\text{calculated}} + \Delta H_{f\mathbf{M}\text{calculated}}];$$
$$\Delta H_{f\mathbf{M}} = -\Delta H_{\mathbf{RX}\text{calculated}} - \Delta H_{f\mathbf{A}\text{experimental}} + \Delta H_{f\mathbf{C}\text{experimental}} + \Delta H_{f\mathbf{D}\text{experimental}} \tag{2}$$

TABLE 3: Calculated Enthalpies for Reaction (B) (ΔH_{rx}; Scheme 2), Enthalpy of Formation (ΔH_f), and Respective Errors for γ-Butyrolactone ($\Delta\Delta H_f$ and $\Delta\Delta H_{rx}$; kcal mol^{-1})[a]

model	ΔH_{rx}	$\Delta\Delta H_{rx}$	ΔH_f	$\Delta\Delta H_f$
B3LYP/6-31+G(d,p)	25.17	0.53	−87.78	0.55
B3LYP/*aug*-cc-pVTZ	24.62	−0.02	−87.21	−0.02
B3LYP/6-311G(d,p)	25.54	0.60	88.13	0.90
B3LYP/6-311+G(d,p)	23.60	−1.34	86.19	−1.04
CBS-4	26.17	1.53	−88.76	1.53
G2	26.37	1.73	−88.96	1.73
G2(MP2)	26.00	1.36	−88.59	1.36
CBS-Q	26.53	1.89	−89.12	1.89
G3	26.65	2.01	−89.24	2.01
*m*PW1PW91/6-31+G(d,p)	24.83	0.19	−87.42	0.19
*m*PW1PW91/6-31++G(d,p)	24.79	0.15	−87.38	0.15
PBE1PBE/6-31+G(d)	24.28	−0.36	−86.87	0.36
PBE1PBE/6-31+G(d,p)	24.69	0.05	−87.28	0.05
PBE1PBE/6-31++G(d,p)	24.65	0.01	−87.24	0.01
PBE1PBE/*aug*-cc-pVDZ	24.38	−0.26	−86.97	0.26
PBE1PBE/*aug*-cc-pVTZ	25.64	1.00	−88.23	1.00
PW91PW91/6-31+G(d,p)	24.63	−0.01	−87.21	−0.02
PW91PW91/6-31++G(d,p)	24.56	−0.08	−87.15	−0.08
MP2/6-31+G(d)	25.53	0.89	−88.13	0.90
MP2/6-31+G(d,p)	25.24	0.60	−87.83	0.60
MP2/6-31++G(d,p)	24.99	0.35	−87.58	0.35
MP2/*aug*-cc-pVDZ	25.69	1.05	−88.29	1.09
B3P86/6-31G(d,p)	26.53	1.89	−89.12	1.89
B3P86/6-31+G(d,p)	24.69	0.05	−87.29	0.06
B3P86/6-31++G(d,p)	24.66	0.02	−87.23	0.02
B3P86/*aug*-cc-pVDZ	23.79	−0.85	−86.38	0.85

[a] ΔH_{rx}(exp) = 24.64 kcal mol^{-1}.

TABLE 4: Calculated Enthalpies for Reaction (C) (ΔH_{rx}; Scheme 2), Enthalpy of Formation (ΔH_f), and Respective Errors for 2-Pyrrolidinone (kcal mol^{-1})[a]

model	ΔH_{rx}	$\Delta(\Delta H_{rx})$	ΔH_f	$\Delta(\Delta H_f)$
B3LYP/6-31+G(d,p)	7.55	−1.89	−45.29	−1.89
B3LYP/6-31++G(d,p)	7.48	−1.96	−45.22	−1.95
B3LYP/*aug*-cc-pVTZ	7.87	−1.57	−45.61	−1.57
B3P86/6-31+G(d)	7.65	−1.79	−45.40	−1.78
B3P86/6-31+G(d,p)	7.84	−1.60	−45.58	−1.59
B3P86/6-31++G(d,p)	8.73	−0.71	−46.47	0.71
B3P86/*aug*-cc-pVDZ	7.68	−1.76	−45.42	−1.76
B3P86/*aug*-cc-pVTZ	8.52	−0.92	−46.16	−1.02
PBE1PBE/6-31+G(d,p)	7.80	−1.64	−45.54	−1.64
PBE1PBE/6-31++G(d,p)	7.77	−1.67	−45.51	−1.67
MP2/6-31G(d)	10.30	0.86	−48.05	0.87
MP2/6-31+G(d)	10.52	1.08	−48.26	1.08
MP2/6-31G(d,p)	9.51	0.07	−47.25	0.08
MP2/6-31+G(d,p)	10.98	1.54	−48.72	1.54
MP2/6-31++G(d,p)	10.98	1.54	−48.72	1.54
MP2/*aug*-cc-pVDZ	11.16	1.72	−48.90	1.72
PW91PW91/*aug*-cc-pVTZ	9.18	−0.26	−46.92	−0.26
mPW1PW91/*aug*-cc-pVTZ	8.55	−0.89	−46.29	0.89
G3	10.60	1.16	−48.34	1.16
G2	10.40	0.96	−48.15	−0.97
G2(MP2)	10.28	0.84	−48.02	−0.84
CBS-Q	10.96	1.52	−48.70	−1.52
CBS-4	10.62	1.18	−48.36	−1.18

[a] ΔH_f(exp) = −47.17 ± 0.73 kcal mol^{-1}.[56]

Results and Discussion

Enthalpy of Formation. *γ-Butyrolactone.* To calculate the enthalpy of formation of γ-butyrolactone, we proposed an isodesmic (A) and a homodesmic (B) reaction. In their studies, Ventura and Segovia used a larger number of isodesmic reactions for a given compound, aiming at finding out which reaction would lead to the best results.[7]

Parameters obtained with the DFT methods were the most accurate compared to those calculated by means of the composite chemical models, with errors smaller than 1.0 kcal

TABLE 5: Proton Affinity (PA, kcal mol^{-1}) Calculated for γ-Butyrolactone (Scheme 3)[a]

model	$H_{neutral}$	$H_{protonated}$	PA	ΔPA
B3LYP/6-31G(d)	−306.387465	−306.708062	202.66	1.86
B3LYP/6-31+G(d,p)	−306.409660	−306.728011	201.25	0.45
B3LYP/6-31++G(d,p)	−306.409756	−306.728136	201.27	0.47
B3LYP/*aug*-cc-pVDZ	−306.431324	−306.749583	201.19	0.39
B3P86/6-31G(d)	−307.215017	−307.535231	202.42	1.62
B3P86/6-31+G(d,p)	−307.233537	−307.553325	202.15	1.35
B3P86/6-31++G(d,p)	−307.233630	−307.553462	202.18	1.38
B3P86/*aug*-cc-pVDZ	−307.257930	−307.577934	202.29	1.49
PBE1PBE/6-31G(d)	−306.046030	−306.365702	202.08	1.28
PBE1PBE/6-31+G(d,p)	−306.065197	−306.384521	201.86	1.06
PBE1PBE/6-31++G(d,p)	−306.065295	−306.384661	201.89	1.09
PBE1PBE/*aug*-cc-pVDZ	−306.090350	−306.600118	202.35	1.55
PW91PW91/6-31+G(d,p)	−306.303775	−306.620091	199.97	−0.83
PW91PW91/6-31++G(d,p)	−306.303896	−306.620243	199.99	−0.81
MP2/6-31G(d,p)	−305.505988	−305.827412	203.18	2.38
MP2/6-31+G(d,p)	−305.524348	−305.838072	198.34	−2.45
MP2/6-31++G(d,p)	−305.525135	−305.838950	198.40	−2.40
*m*PW1PW91/6-31+G(d,p)	−306.331186	−306.651597	202.54	1.74
*m*PW1PW91/6-31++G(d,p)	−306.331287	−306.651743	202.57	1.77
G2	−305.995758	−306.312573	200.28	−0.51
G2(MP2)	−305.988283	−306.305440	200.50	−0.30
CBS-Q	−306.006712	−306.322617	199.71	−1.09
G1	−305.992515	−306.307878	199.37	−1.43
CBS-QB3	−306.009009	−306.324592	199.51	−1.29
B98/6-31+G(d)	−306.283612	−306.598717	199.21	−1.59
B98/6-31+G(d,p)	−306.291404	−306.612307	202.85	2.05
B98/6-31++G(d,p)	−306.291499	−306.612437	202.87	2.07
B98/*aug*-cc-pVDZ	−306.316625	−306.637506	202.84	2.04

[a] PA(exp) = 200.8 kcal mol^{-1}.[56]

TABLE 6: Gas-Phase Basicity (GB) for γ-Butyrolactone (Scheme 3), and the Differences Compared to the Experimental Value (ΔGB; kcal/mol), at 298 K and 1 atm[a]

model	$G_{neutral}$	$G_{protonated}$	GB	ΔGB
B3LYP/6-31+G(d,p)	−306.444417	−306.763122	193.71	0.61
B3LYP/6-31++G(d,p)	−306.444517	−306.763254	193.73	0.63
B3LYP/*aug*-cc-pVDZ	−306.466133	−306.784763	193.66	0.56
B3P86/6-31G(d)	−307.249670	−307.570236	194.88	1.78
B3P86/6-31+G(d,p)	−307.268225	−307.588346	194.60	1.50
B3P86/6-31++G(d,p)	−307.268323	−307.588490	194.63	1.53
B3P86/*aug*-cc-pVDZ	−307.292667	−307.613003	194.73	1.63
PBE1PBE/6-31+G(d,p)	−306.099837	−306.419484	194.30	1.20
PBE1PBE/6-31++G(d,p)	−306.099941	−306.419632	194.33	1.23
PW91PW91/6-31+G(d,p)	−306.338663	−306.655322	192.43	−0.67
PW91PW91/6-31++G(d,p)	−306.338788	−306.655484	192.45	−0.65
PW91PW91/*aug*-cc-pVDZ	−306.362782	−306.679405	192.40	−0.69
mPW1PW91/6-31+G(d)	−306.357946	−306.672763	191.27	−1.83
mPW1PW91/6-31+G(d,p)	−306.365831	−306.686569	194.99	1.89
mPW1PW91/6-31++G(d,p)	−306.365937	−306.686723	195.02	1.92
mPW1PW91/*aug*-cc-pVDZ	−306.391206	−306.712110	195.09	1.99
G1	−306.027458	−306.343242	191.88	−1.22
G2	−306.030701	−306.347936	192.79	−0.31
G2(MP2)	−306.023227	−306.340804	193.00	−0.10
CBS-Q	−306.041499	−306.357788	192.19	−0.90
CBS-4	−306.094830	−306.409527	191.20	−1.90
CBS-QB3	−306.043790	−306.359709	191.96	−1.14
B98/6-31+G(d)	−306.318364	−306.633821	191.67	−1.43
B98/6-31+G(d,p)	−306.326167	−306.647419	195.31	2.21

[a] GB(exp) = 193.10 kcal mol^{-1}.

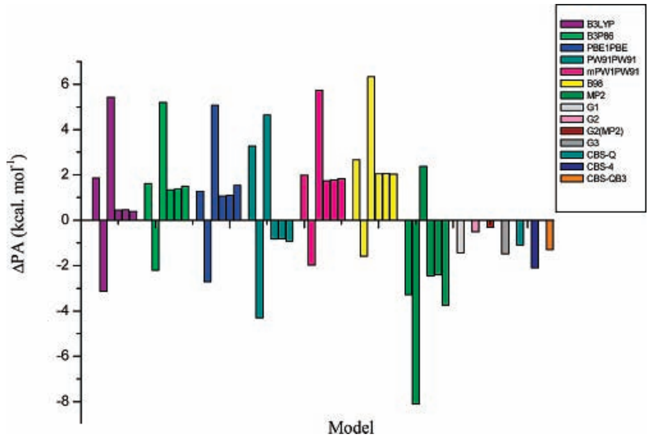


Figure 1. Plot of proton affinity error (ΔPA = PA_{exp} − PA_{calcd}), in kcal mol^{-1}, of γ-butyrolactone as determined by the different methods and basis sets employed in this work. The basis sets are ordered as 6-31G(d); 6-31+G(d); 6-31G(d,p); 6-31+G(d,p); 6-31++G(d,p); and aug-cc-pVDZ.

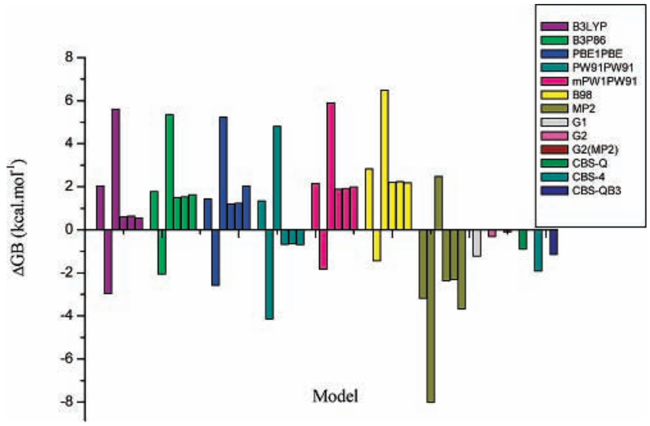


Figure 2. Plot of gas-phase basicity error (ΔGB = GB_{exp} − GB_{calcd}), in kcal mol^{-1}, for γ-butyrolactone as determined by the different methods and basis sets employed in this work. The basis sets are ordered as 6-31G(d); 6-31+G(d); 6-31G(d,p); 6-31+G(d,p); 6-31++G(d,p); and aug-cc-pVDZ.

mol^{-1} for the former (Tables 2 and 3 and the Supporting Information, Tables S2 and S3). The use of diffuse functions increased the accuracy of the methods B3LYP and B3P86, because the results obtained with the basis sets 6-31G(d) and 6-31G(d,p) were less accurate than those achieved with the basis sets 6-31+G(d,p) and 6-31++G(d,p). The same behavior was observed in the case of the methods PW91PW91 *m*PW1PW91. So, among the DFT models, the most accurate enthalpies of formation were obtained with B3LYP, independent of the polarized and diffuse basis set employed.

The composite chemical models G3, G2 ,G2(MP2), and CBS-Q revealed absolute errors larger than 2 kcal mol^{-1}, even though they were developed to reproduce thermochemical data with high accuracy.

The errors for the enthalpy of reaction B were of the same magnitude as those obtained for the enthalpy of formation of γ-butyrolactone. Therefore, molecules that do not have reported experimental values for their enthalpy of formation or for those compounds whose values are not accurate; the enthalpy of formation could be estimated by considering the magnitude of the errors of the reaction enthalpy. The models B3P86/6-31++G(d,p) B3P86/6-31+G(d,p), PBE1PBE1/6-31++G(d,p), and PBE1PBE1/6-31+G(d,p) were the most accurate. The largest deviations from the experimental values were observed for the basis sets without diffuse functions for DFT and MP2 methods. As in the case of reaction A, the method B3LYP also led to values of enthalpy of formation close to the experimental ones. The best results were achieved using the basis sets 6-31+G(d,p) and *aug*-cc-pVTZ. The use of 6-311 basis set on B3LYP method led to less accurate values for enthalpies of formation than 6-31 basis set and *aug*-cc-pVTZ (see Tables 2 and 3 and the Supporting Information, Tables S2 and S3).

2-Pyrrolidinone. To better understand the use of theoretical models for the obtention of thermochemical parameters, in this section we will discuss the results obtained for 2-pyrrolidinone (Table 4 and the Supporting Information, Table S4). Table 4

TABLE 7: Gas-Phase Basicity (GB) and Proton Affinity (PA) for γ-Butyrolactone, and the Differences Compared to the Experimental Values (ΔGB and ΔPA; kcal/mol), at 298 K and 1 atm[a]

model	H_{neutral}	$H_{\mathrm{protonated}}$	G_{neutral}	$G_{\mathrm{protonated}}$	PA	ΔPA	GB	ΔGB
B3LYP/6-311G(d)	−306.470838	−306.779996	−306.499450	−306.815027	−195.48	5.32	−191.75	1.35
B3LYP/6-311+G(d)	−306.472795	−306.783591	−306.507527	−306.818667	−196.51	4.29	−188.96	4.14
B3LYP/6-311G(d,p)	−306.473019	−306.794628	−306.507731	−306.829680	−203.30	−2.49	−195.74	−2.65
B3LYP/6-311+G(d,p)	−306.480857	−306.797999	−306.515596	−306.833080	−200.49	0.31	−192.94	0.16
B3LYP/6-311++G(d,p)	−306.480953	−306.798150	−306.515695	−306.833247	−200.52	0.28	−192.99	0.11

[a] PA(exp) = 200.8 kcal mol^{-1}; GB(exp) = 193.10 kcal mol^{-1}.

shows the values for the reaction enthalpies, enthalpies of formation and absolute errors lower than 2.0 kcal mol^{-1} for each of the models employed in this work.

It can be seen from Table 4 that the enthalpies of formation of 2-pyrrolidinone obtained using the models MP2/6-31G(d,p), MP2/6-31G(d), B3P86/6-31++G(d,p), PW91PW91/*aug*-cc-pVTZ, *m*PW1PW91/aug-cc-pVTZ, G2, and G2(MP2) were fairly accurate, with the absolute error being less than 1 kcal mol^{-1}. It is difficult to conclude which of the methods was the most accurate on the basis of these results, although the models MP2/6-31G(d), MP2/6-31G(d,p), G2, and G2(MP2) led to similar results. So, the geometry optimization with the method MP2 is important for the obtention of an accurate value for the enthalpy of formation of 2-pyrrolidinone, because the geometry of the models G2 and G2(MP2) is optimized using this method.[15]

Proton Affinity and Gas-Phase Basicity. The models B3P86, B3LYP, and PBE1PBE were the ones that best described the γ-butyrolactone PA values, and the basis sets 6-31+G(d,p) and 6-31++G(d,p) gave the most accurate results (Table 5 and the Supporting Information, Table S5). The least satisfactory DFT results were obtained for the basis set 6-31G(d,p), independent of the method employed. The basis sets with diffuse functions provided the best results for DFT methods when accompanied by polarization functions for all the atoms, including the hydrogens. When the diffuse functions were used on atoms other than hydrogen only, the values obtained for the thermochemical parameters were always underestimated, which is clear from the analysis of the plots in Figure 1. When it comes to composite models, the G2 and G2(MP2) were the most accurate with error closed to −0.51 and −0.30 kcal mol^{-1}, respectively, when compared to the experimental value.

The B3LYP density functional calculates gas-phase proton affinity with high precision for basis of containing first- and second-row atoms. Several works have shown that the performance of B3LYP model is better than other DFT methods at calculating the thermochemical parameters, and in some cases, the B3LYP functional is more accurate then composite models like G2 and G2(MP2). Our results agree with this previous assessment.[58,59] Moreover, the basicity and acidity of ethyl, vinyl, and ethynylarsine were studied by G2 composite model and B3LYP density functional; and the authors conclude that the performance of B3LYP in the description of thermochemical parameters of arsenic moieties is good, when compared to experimental values.[60]

On the one hand, Burk and colleagues tested the B3LYP functional employing various basis sets, and the most accurate acidity and basicity values were obtained with basis sets that use polarized and diffuse functions, which agrees with our results.[61] When diffuse functions were not employed, overestimated thermochemical parameters were achieved. The composite chemical models underestimated the PA experimental results (Table 5 and the Supporting Information, Table S5).

From the plot in Figure 1, one can observe that the basis sets without diffuse functions overestimate the PA values. When a basis set includes diffuse functions, like 6-31+G(d,p), 6-31++G(d,p) and *aug*-cc-pVDZ, the theoretical and experimental values are close. The models B3LYP/6-31+G(d,p), B3LYP/6-31++G(d,p), B3LYP/*aug*-cc-pVDZ, G2, and G2(MP2) furnish the most accurate proton affinity values.

The GB values calculated for γ-butyrolactone are shown in Table 5. Once again, the models B3LYP/6-31+G(d,p), B3LYP/6-31++G(d,p), B3LYP/*aug*-cc-pVDZ, G2, and G2(MP2) gave the best results. All DFT methods with 6-31G(d,p) basis set overestimated the GB values as shown at Figure 2.

Thermochemical parameters, such as ΔH_{f}, PA, and GB, obtained by B3LYP with 6-311G and *aug*-cc-pVTZ basis sets, were used to verify the effects of triple-ζ basis set with or without the addition of polarization or diffuse functions.

The behavior of 6-311 basis set is similar to that for the 6-31 basis set, the results of which can be observed at Table 7. As regards the B3LYP/6-311+G(d,p), B3LYP/6-311++G(d,p), and *aug*-cc-pVTZ models, all results are close.

Although the use of scaling factors is recommended in the computation of vibrational frequencies and zero point energies, ZPE, our studies indicate that the use of these factors always lead to values far from the experimental data. This justifies the values obtained by the CBS models, because they use scaling factors for the computation of vibrational energies. Another attempt at improving our results was to consider the anharmonic vibrational frequencies. However, besides the increase in computational time, the anharmonic corrections reduced the enthalpy of the components of the isodesmic and protonation reactions by approximately 1 kcal mol^{-1}. So, in general, once the energy of all the compounds are calculated, the contribution of anharmonic vibrational frequencies is zero, which is in agreement with the results described by DeYonker and coworkers.[62]

Conclusions

The enthalpies of formation obtained for γ-butyrolactone by the isodesmic reaction (A) were more accurate than those achieved by means of the functionals B3LYP, PW91PW91, PBE1PBE1, and B98 in relation to the composite chemical models G2, G2MP2, and CBS-Q. In the case of the homodesmic reaction (B), the functionals also resulted in more accurate values, where the absolute errors were less than 0.5 kcal mol^{-1} when the basis set 6-31+G(d,p) was used. As for 2-pyrrolidinone, the absolute error of its enthalpy of formation obtained by isodesmic reaction (C) was lower with respect to the experimental value (−47.17 ± 0.73 kcal mol^{-1})[56] in the case of the models MP2/6-31G(d,p) and PW91PW91/*aug*-cc-PVTZ, for which the values were 0.08 and −0.26 kcal mol^{-1}, respectively.

Concerning the proton affinity and gas-phase basicity of γ-butyrolactone, although the composite chemical models G2, and G2(MP2) also led to values close to the experimental ones, −0.51 and −0.30 kcal mol^{-1} for proton affinity, respectively, the models B3LYP/6-31+G(d,p), B3LYP/6-31++G(d,p), and B3LYP/*aug*-cc-pVDZ gave more satisfactory results, with absolute errors of 0.45, 0.47, and 0.39, respectively. Still with relation to proton affinity, the basis set 6-31G(d,p) overestimated the values, thus contributing to an increase in the absolute mean error. As for gas-phase basicity, the basis set 6-31+G(d) resulted in underestimated values compared to the experimental data, independent of the method employed.

The divergent results obtained with the various methods used in the computation of the thermochemical parameters in this work should result in tests leading to more accurate methods for a given class of molecules. Though the obtained results by some methods are very close to experimental values, the number of compounds tested was small and the conclusions should not be generalized to other classes of compounds.

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Supporting Information Available: The enthalpies of formation at 298.15K for all anchor compounds at isodesmic reactions. The enthalpies of formation, absolute errors, enthalpies of reactions for DFT methods, and ab initio composite for isodesmic reactions A, B, and C. All results obtained for computed proton affinity and gas-phase basicity to the γ-butyrolactone (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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