Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 109 (2005) 195–204

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Estimating thermochemical properties of hydroprocessing reactions by molecular simulation and group contribution methods

Krishnaswamy Rajagopal[a,*], Victor Ruiz Ahón[a], Esteban Moreno[b]

[a] Escola de Química, UFRJ, CEP 21949-900, Rio de Janeiro, RJ, Brazil
[b] CETEM, CEP 21949-900, Rio de Janeiro, RJ, Brazil

Abstract

The standard enthalpy of formation, estimated by the group contribution method of Benson, and by semi-empirical molecular simulation methods has been compared with experimental data. Benson's method estimates hydrocarbon enthalpies satisfactorily. The Benson's estimates of enthalpies of free radicals are in general superior to the molecular simulation parameterization method (PM3) and are less accurate than the specialized computationally intensive PM3-family correlation (PM3-FC) method. The estimation of enthalpies for hydrocarbon radicals is substantially improved by a linear correlation of estimated values from semi-empirical molecular simulation method PM3 with experimental data. The radical enthalpies are now comparable to molecular simulated PM3-FC estimates. The hydrocarbon cations were divided into classes and estimated enthalpies found by adding Benson's enthalpy of radicals to the average ionization energy for the class. These predictions have an average absolute deviation of 8.6 kcal mol^{-1}. The proposed correlations effectively predict the standard enthalpy of formation of hydrocarbons, free radicals and carbocations. This methodology can be readily implemented in simulation programs to estimate thermochemical properties of hydrocarbons, free radicals and carbocations and to improve the design and optimization of hydroprocessing units reducing costly hydrogen consumption.

Keywords: Enthalpy; Free radicals; Carbocations; Group contribution; Molecular simulation; Property estimation; Thermochemistry; Hydrocracking

1. Introduction

The refining of heavy oil and of petroleum residues generally involves carbon removal and/or hydrogen addition in a manner that the yield of cross-linked dehydrogenated toluene insoluble residues (coke) can be reduced in favor of enhanced yields of liquid products with a higher atomic hydrogen/carbon ratio. For this purpose, hydrocracking processes where cracking occurs simultaneously with hydrogenation of the products are widely employed. The combination of desulfurized and denitrogenated lighter products of lower overall aromaticity makes hydrocracking an ideal refinery process for producing middle distillates, diesel, jet and gas turbine fuels meeting the more stringent fuel specifications.

The hydrocracking processes are becoming increasingly important in the economic performance of petroleum refining operations, especially in heavy oil processing. The heavy oils and petroleum residues of distillation contain a complex mixture of five- and six-membered ring naphthenes which often have multiple alkyl constituents and which may be joined to one another or fused to aromatic rings. These components of heavy oils are responsible for a series of problems during refining, like increased coke formation, deactivation or poisoning of the catalyst, which raises the operational costs [1]. Moreover, the world demand for middle distillates continues to grow while that of coke is decreasing.

Hydroprocessing can be conducted under a variety of operating conditions. Hydrotreating is operated under relatively mild conditions with essentially no changes in molecular size distribution. It refers to a variety of catalytic hydrogenation processes, which saturate unsaturated hydrocarbons and remove S, N, O and metals from various petroleum streams in a refinery. Hydrocracking, on the other hand, not only removes N, S and metals but also leads to cracking of hydrocarbons to give lighter products under much more severe conditions. More than 50% of the feed has its molecular size

---

* Corresponding author. Tel.: +55 21 2562 7654; fax: +55 21 2562 7424.
E-mail address: raja@eq.ufrj.br (K. Rajagopal).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.08.020

Nomenclature

a, b	constants for linear correlation
EA	electron affinity
e^-	electron
f_j	weight factor for group j
H	hydrogen atom
$h\nu$	photoionization energy
ΔH_f^0	standard enthalpy of formation (kcal mol^{-1}) (at 298 K)
IE	ionization energy (kcal mol^{-1})
$R^\bullet$	hydrocarbon radical
R^+	carbocation
RH	hydrocarbon molecule
R^2	coefficient of determination

Superscript

0	standard state
GC	group contribution
PM3	parameterization method, PM3 (a semi-empirical molecular simulation)

Subscript

c	calculated by Benson's or PM3 molecular simulation method
e	experimental
f	formation
i	component
PM3	semi-empirical molecular simulation method, PM3
thresh	ionization threshold energy
+	indicates positive charge, a cation
−	indicates negative charge, an anion
rxn	reaction
acid	reaction in acid environment

distribution reduced. Mild hydrocracking or hydroconversion is a process variant in which there is less than 30% change in molecular size distribution. This process has recently become popular because the moderate conditions under which it is performed enabling the use of existing hydrotreating reactors but still results in some conversion to lighter products. Thus, operational and capital costs can be lowered substantially [2]. In hydroconversion, the additional hydrogen and operating costs to adjust the product slate has to be considered carefully. The efficient conversion of heavy oil by hydrotreating or by fluid catalytic cracking requires serious efforts to develop adequate catalysts as well as the modification of existing process or the development of new processes [3,4].

Based on cracking mechanism, there are two main hydroconversion processes: catalytic hydrocracking and hydrothermal cracking. The catalytic hydrocracking processes are relatively mature technologies and are applied to a wide variety of fractions of petroleum. The operating temperature is in the range 340–420 °C and usually high pressures are required for conversions involving several reaction mechanisms. The mechanism of catalytic hydrocracking of the carbon–carbon bond proceeds through carbocation facilitated by interaction with strong acids [5]. This process utilizes bifunctional catalysts increasing the H/C ratio by hydrogenation promoted with a metal or a metal sulfide and simultaneous reduction of molecular weight by a cracking function, typically by a zeolite.

The thermal hydrocracking does not have the limitations associated with the presence of catalyst and can be conducted at operating temperatures above 430 °C. In such cases, the rupture of the carbon–carbon bond occurs through free radical formation due to high temperatures (thermolysis) or through the radicals initiators formed by decomposition of feed [6,7]. Thermal conversions produce less valuable products, when compared to the catalytic hydrocracking, and thus they usually require further processing. The coke formation, for example, can exceed 20% (w/w) for heavy oil feed stocks and the products still maintain the major part of the original heteroatoms (sulfur and nitrogen) and metal (nickel, vanadium and iron) compounds [3].

Most of the literature dealing with hydrocracking processes concentrates on coke reduction, through the use of a hydrogen donor or in the development of new catalysts for the heteroatom removal. However, comparatively, little published work is available to understand the thermochemistry of the process for the purpose of producing more middle distillates (more liquid products). No really new technology for the processing of residues has emerged during the last few years [8], although several lumping methods for describing process kinetics seems to achieve some success in understanding hydrocracking in industrial scale [9–12].

In order to develop new processes as well as to design and optimize the hydroprocessing units, it is essential to estimate thermochemical properties of substances, carbocations and free radicals accurately by simple methods, besides developing mechanistic and kinetics models that represent cracking reactions of heavier fractions [9]. In simulations, around 70% of the computational time is spent in estimating physical–chemical properties [13]. Therefore, the methods should be simple enough for repetitive calculations. These properties are also useful in determining reaction pathways, estimating kinetic constants, chemical equilibrium conditions and energy balances. These estimated thermochemical properties are used in simulating and correlating kinetics of pyrolysis of distillation residues [14–16].

For estimating physical properties, the group contribution methods are simple to use and can be readily incorporated in the simulation of chemical processes. The molecular simulation methods however can represent the structure, energy levels and interactions more correctly. It is worthwhile comparing these methods for a specific objective in mind like hydrocracking processes.

The objective of this work is to improve the accuracy and facility in estimating the standard-state enthalpy of formation for substances, free radicals and carbocations involved in hydrocracking processes and, in particular, to compare systematically the estimates obtained by group contribution methods (Joback and Benson) and by molecular simulation methods (parameterization method, PM3 and PM3-family correlation, PM3-FC) of different complexity.

2. Methodology

In this work, a computational program was implemented in order to estimate the standard-state enthalpy of formation (ΔH_f^0) for substances and free radicals. This program is based on the Benson's group contribution method [17]. We also propose approximate methods for quickly estimating ionization energies of free radicals and enthalpy of formation of carbocations. The estimates of the enthalpy of formation by group contribution methods and by semi-empirical molecular simulation methods were compared with experimental values from the literature.

The formation enthalpies of substances, radicals and carbocations were calculated as follows.

2.1. Substances and radicals

Standard enthalpies of formation at 298 K of several pure substances were calculated, for 63 hydrocarbons and 14 aromatics by the following methods recommended in the literature:

- The group contribution method of Joback and Reid [18].
- The group contribution method of Benson [17].
- The molecular simulation method, PM3 using the commercial software Titan [19].

The group contribution calculations can be schematically represented as:

$$\Delta H_f^{GC} = \sum_i f_i (\Delta H_f^0)_i \qquad (1)$$

where the sum is over all the groups present for both Benson [17] and Joback and Reid [18] methods. For radicals only Benson's method is available in the literature. The enthalpy of formation of substances and free radicals were also calculated using the semi-empirical molecular simulation method PM3:

$$\Delta H_f^{MS} = f(E_{PM3}) \qquad (2)$$

The calculated values ΔH_f^{GC} and ΔH_f^{MS} were then compared with the experimental values [20]. Similarly, the standard enthalpies of formation of several families of radicals were calculated using the group contribution method of Benson and the molecular simulation method PM3 using the commercial software Titan [19]. The values were compared with the molecular simulation calculations done using Mopac software as well as with the evaluated experimental values reported by Ma and Schoebert [21].

The values obtained by Benson's group contribution method, the molecular simulation method PM3 using the commercial softwares Titan and Mopac, were linearly regressed with experimental standard-state enthalpy of formation for free radicals to improve the accuracy.

$$\Delta H_f^0 = a(\Delta H_f^{Benson}) + b \qquad (3a)$$

$$\Delta H_f^0 = a(\Delta H_f^{PM3}) + b \qquad (3b)$$

2.2. Carbocations

In the case of carbocations, there is no readily available group contribution method for estimating enthalpy of formation. In hydrocracking mechanism, in a simplified view, there are either carbocations species derived from the protolytic addition (RH_2^+) or from hydride removing (R^+) [26]. The last one is the most common of them and it is the only one investigated in this article.

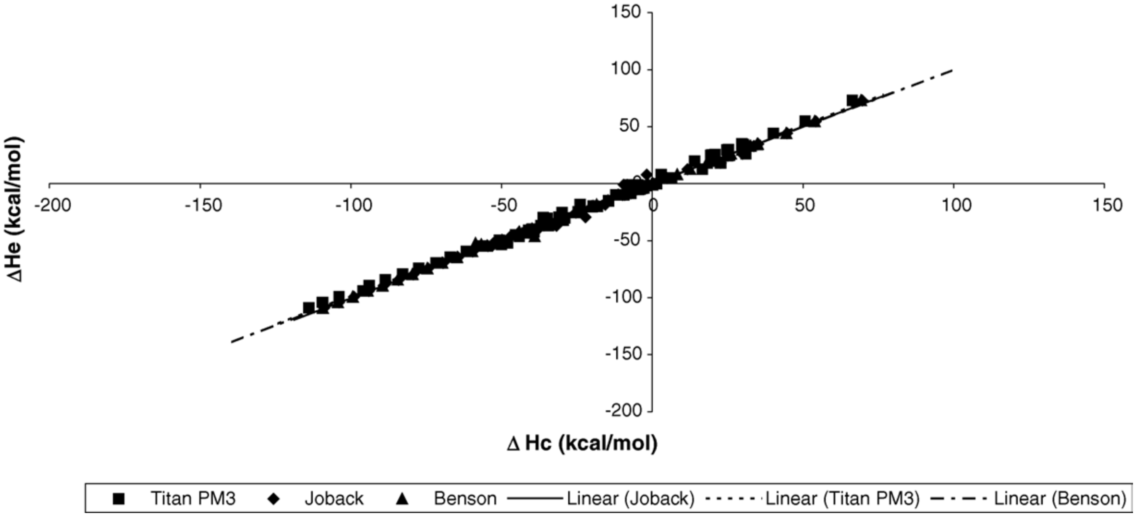

Fig. 1. Enthalpy of formation of hydrocarbons at 298 K (kcal mol^{-1}).

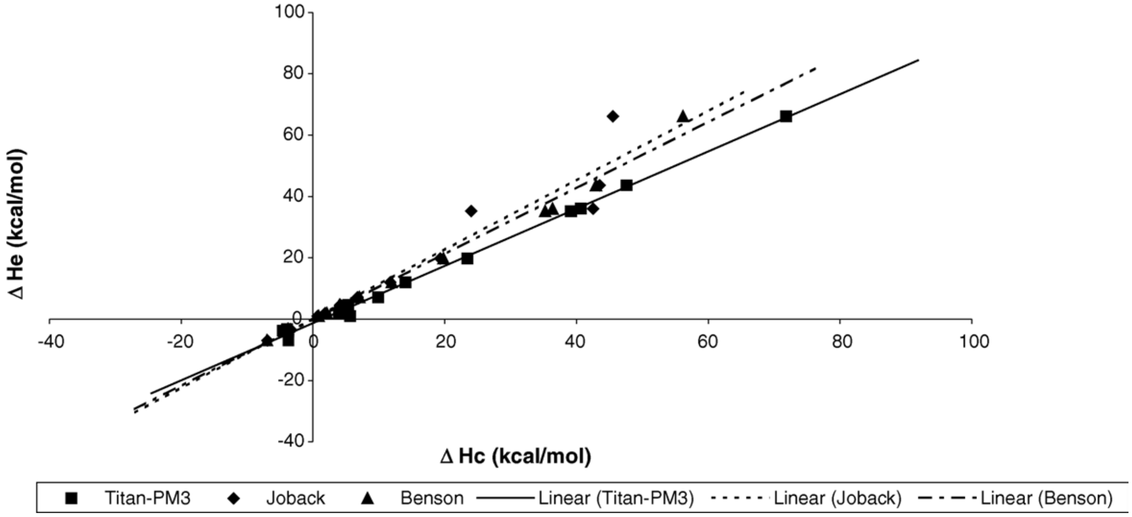

Fig. 2. Enthalpy of formation of aromatics at 298 K (kcal mol^{-1}).

The enthalpy of formation of carbocation at 298 K can be determined from enthalpy of formation of its corresponding radical:

$$R^{\bullet} + h\nu \rightarrow R^{+} + e^{-} \tag{4}$$

The enthalpies are related by:

$$\Delta H_f^0(R^{+}) = \Delta H_f^0(R^{\bullet}) + IE_0(R^{\bullet}) + [\text{thermal corrections}] \tag{5}$$

The thermal corrections are usually less than 0.3 kcal mol^{-1} and can be neglected [22]. We estimate the enthalpy of formation of radicals $\Delta H_f^0(R^{\bullet})$ by Eqs. (3a) and (3b). The second experimental quantity needed for our purpose in Eq. (5), the adiabatic ionization energy IE_0, is the lowest energy required to remove an electron from the radical in the gas phase. It is the difference between the ground state energy of the ion formed and the energy of the original atom, molecule, radical or ion.

3. Results and discussion

3.1. Substances and radicals

To improve the accuracy of estimation of enthalpies of formation for hydrocarbons and for aromatic substances, the calculated values were linearly regressed with the experimental values for each class of substances. The parity between estimated and experimental values is shown in Figs. 1 and 2. The linear constants *a*, *b* and the coefficient of determination (R^2) are also shown in Tables 1 and 2. The results for primary radicals are shown in Fig. 3. Fig. 4 shows the results for

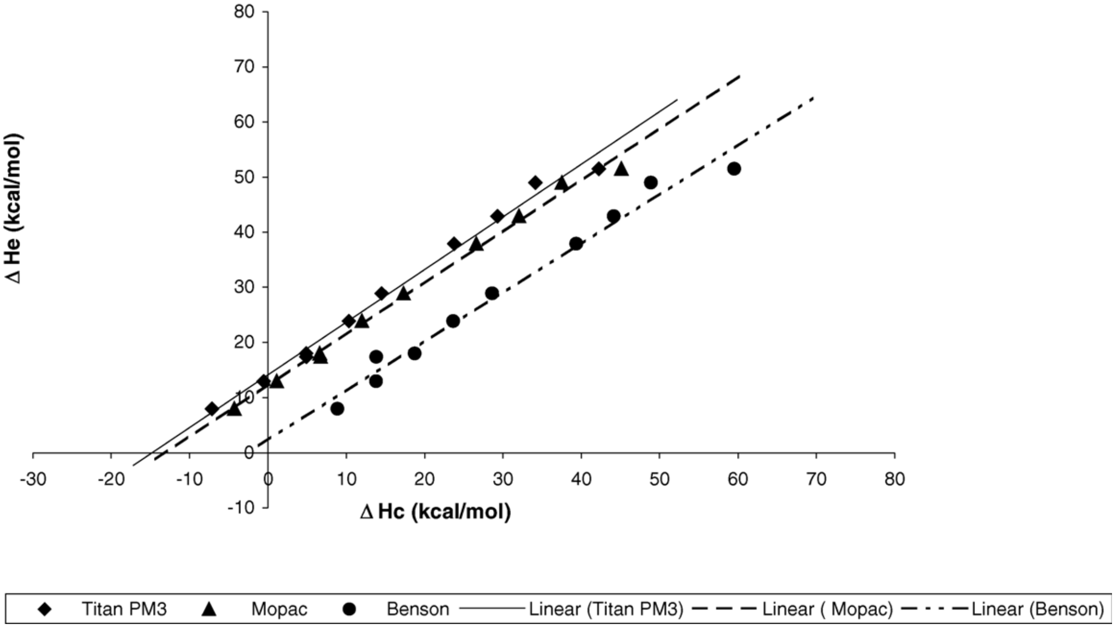

Fig. 3. Enthalpy of formation of primary radicals at 298 K (kcal mol^{-1}).

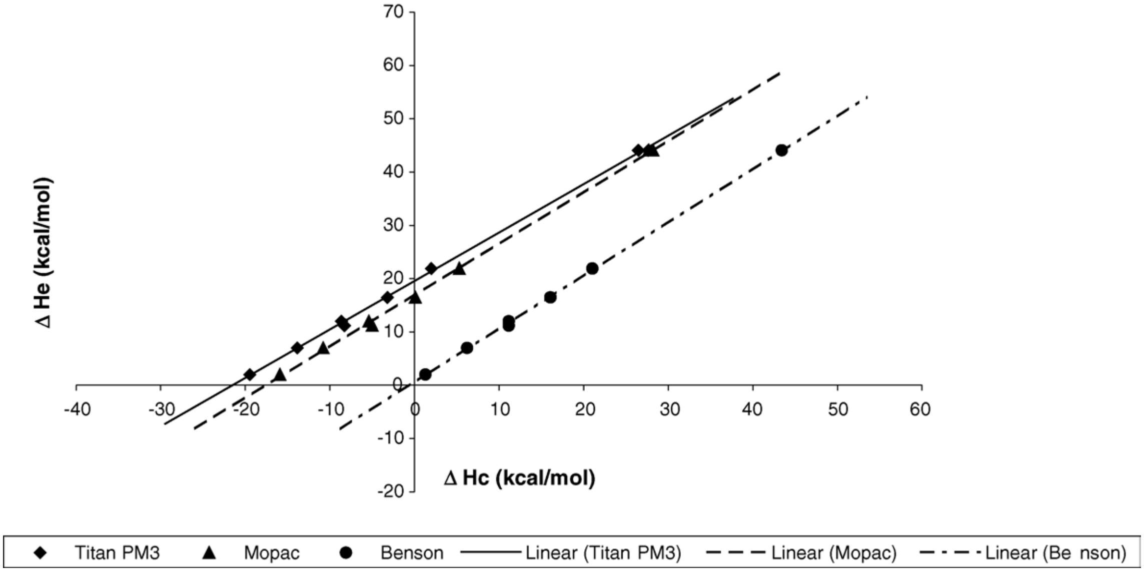

Fig. 4. Enthalpy of formation of secondary radicals at 298 K (kcal mol^{-1}).

secondary radicals. Similarly, Fig. 5 compares the results for tertiary radicals. Fig. 6 exhibits results for alken-α radicals. Fig. 7 compares the results for cycloalkyl-α radicals and Fig. 8 shows results for aryl radicals.

In Tables 1–3, the estimates from the proposed correlations (Eqs. (3a) and (3b)) are compared with experimental values for each class of radicals. The coefficients and correlation (a, b and R^2) estimated for the Benson's, Titan PM3 and Mopac PM3

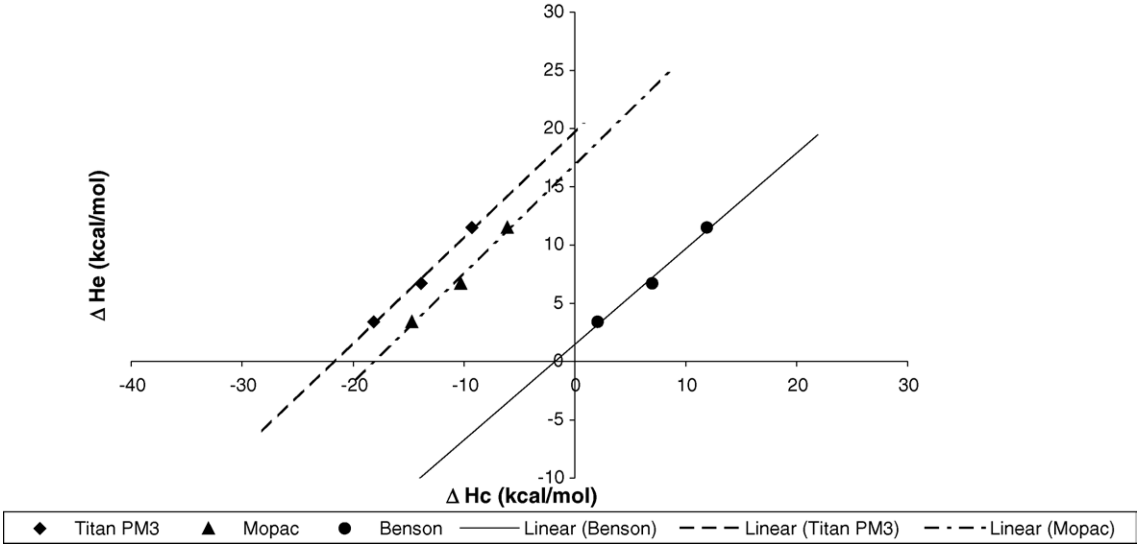

Fig. 5. Enthalpy of formation of tertiary radicals at 298 K (kcal mol^{-1}).

Table 1
Average absolute deviations for estimation of free radical enthalpies (kcal mol^{-1}) and correlation coefficients for the Benson method

Radical	Benson	Mopac PM3-FC	Benson correlated			
			AAD[a]	a	b	R^2
Primary	1.7320	0.7900	1.6403	1.0076	−0.7222	0.9986
Secondary	0.6200	0.4000	0.2416	1.0020	0.4821	0.9987
Tertiary	0.6767	0.4667	1.2005	0.9965	−0.9461	0.9915
Alken-α-yl	2.9336	2.6000	3.7084	0.9420	2.0598	0.9934
Cycloalkyl	1.7050	2.8250	1.6876	0.9965	−0.9461	0.9915
Aryalk-α-yl	0.7967	0.4333	0.6340	0.9966	−0.6557	0.9894

[a] AAD: average absolute deviation.

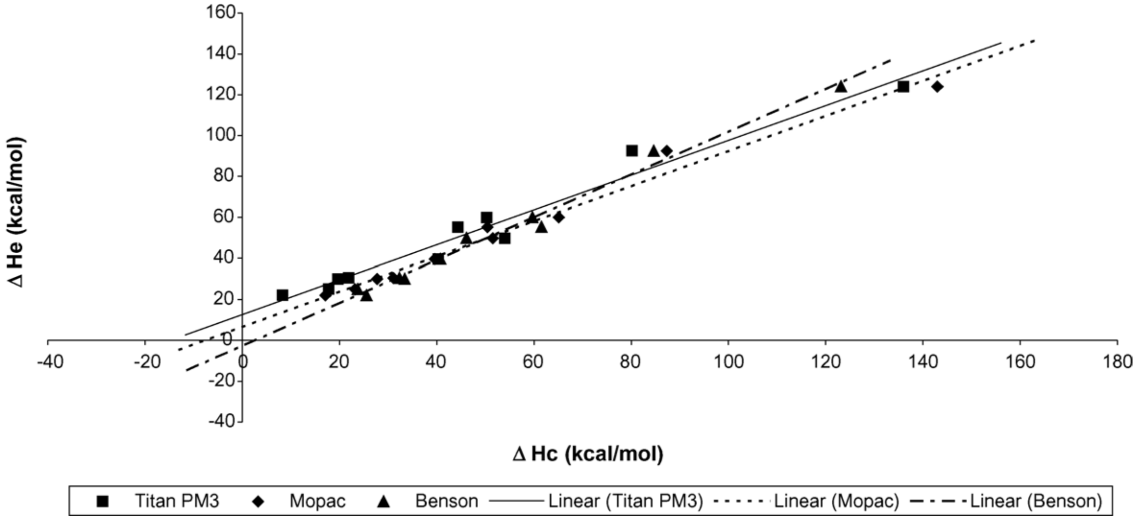

Fig. 6. Enthalpy of formation of alken-α radicals at 298 K (kcal mol^{-1}).

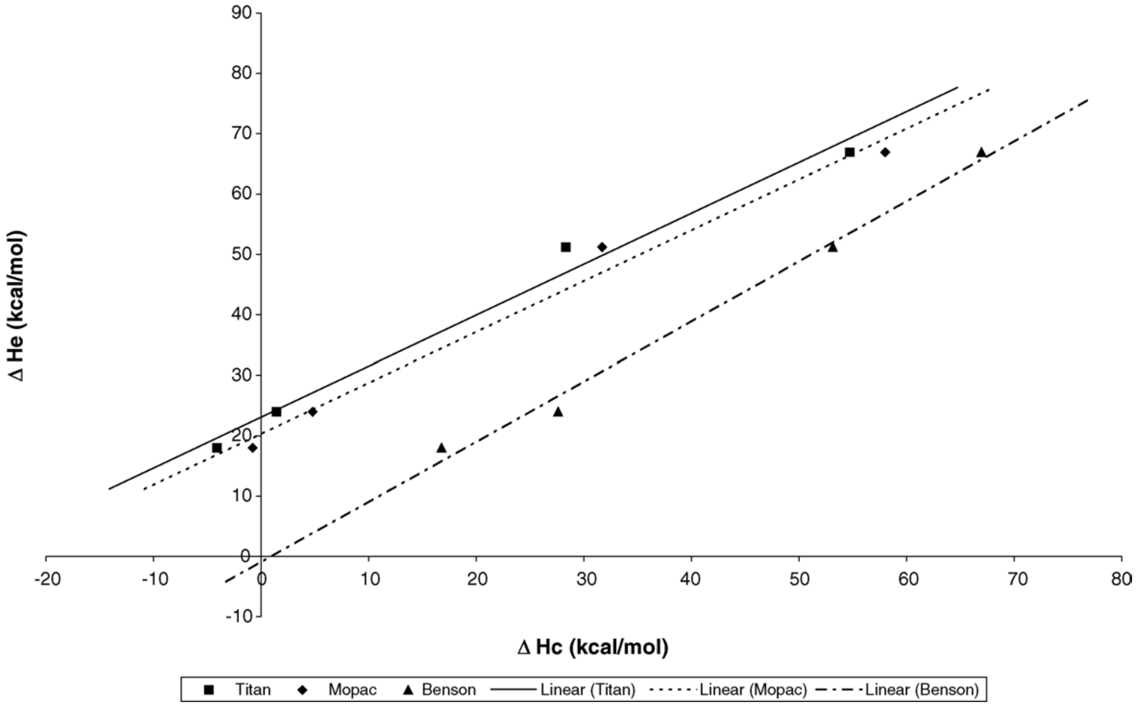

Fig. 7. Enthalpy of formation of cycloalkyl-α radicals at 298 K (kcal mol^{-1}).

Table 2
Average absolute deviations for estimation of free radical enthalpies (kcal mol^{-1}) and correlation coefficients for the Titan PM3 method

Radical	Titan PM3	Mopac PM3-FC	Titan PM3 correlated			
			AAD[a]	*a*	*b*	R^2
Primary	13.4128	0.7900	1.1052	0.9727	14.0360	0.9924
Secondary	19.5089	0.4000	0.3717	0.9071	19.5820	0.9991
Tertiary	20.9707	0.4667	3.5455	0.8212	22.0540	0.9993
Alken-α-yl	8.9408	2.6000	8.6737	0.8723	19.7590	0.9915
Cycloalkyl	19.9310	2.8250	2.1145	0.8432	23.0820	0.9837
Aryalk-α-yl	8.0723	0.4333	0.9329	0.5331	23.0420	0.9761

[a] AAD: average absolute deviation.

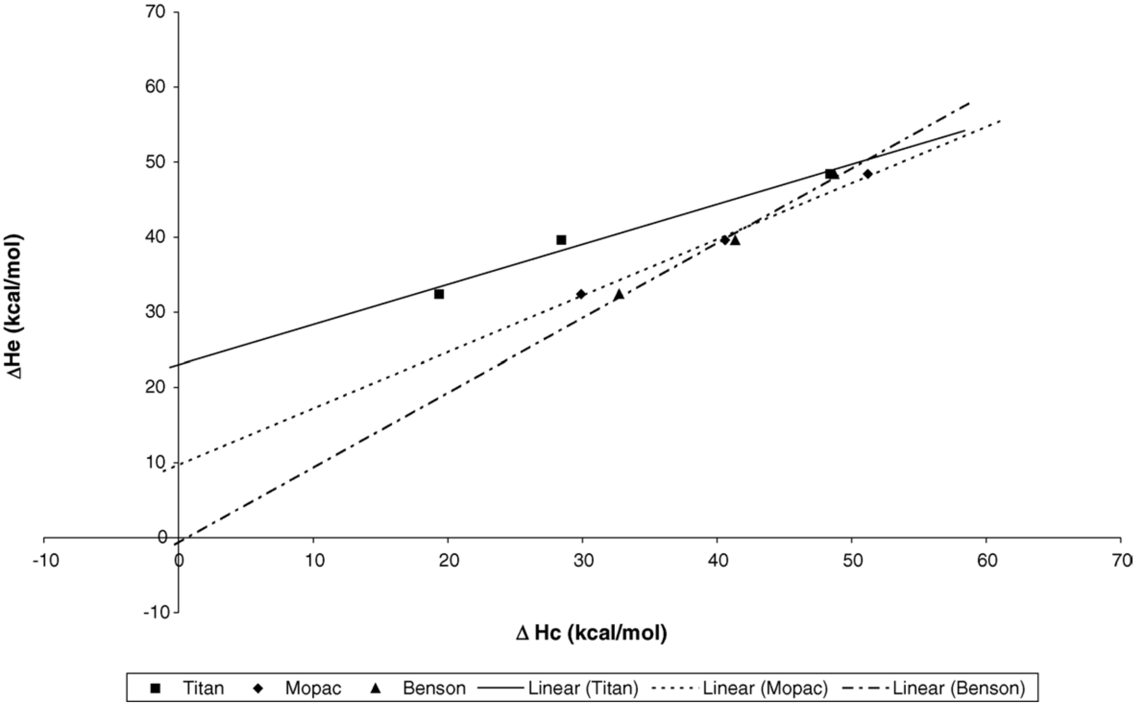

Fig. 8. Enthalpy of formation of aryl radicals at 298 K (kcal mol^{-1}).

methods are also given. Additionally, results obtained using a specialized molecular simulation method, which demands a high computational effort [21], Mopac PM3-FC, are included. The estimates show excellent linear correlation with experimental values. The average absolute deviations (AAD) exhibit a substantial reduction when using the linear correlations for Titan PM3 and Mopac PM3 methods except for the tertiary and the alken-α-yl radicals, where little experimental data is available. For Benson's group contribution method, the deviations (AAD) reduced to a lesser extent. Simple and approximate molecular simulation along with present correlations could be used to estimate, with some accuracy, enthalpy of formation of free radicals that are not available in [21].

3.2. Carbocations

As exposed in the methodology, for the estimation of the enthalpy of carbocations ($\Delta H_f^0(R^+)$)) we need the enthalpy of formation of radicals ($\Delta H_f^0(R^\bullet)$) and sum with the adiabatic ionization energy of radicals (IE_0) (Eq. (5)). The enthalpy of free radicals has been estimated with Benson's method (Eqs. (3a) and (3b)). The proposed linear correlation can also be used in the case of semi-empirical PM3 molecular simulation instead of Benson's method.

Using ion cyclotron resonance mass spectrometry several direct experimental measurements of adiabatic ionization energy have been made recently by ionizing a free radical to a carbocation. Lias et al. [23] have collected and reviewed extensively experimental ionization energy of radicals. The standard adiabatic ionization energy of radicals is presented in a convenient form in their thermochemical databank.

From ionization energy values of 41 hydrocarbon radicals obtained in the literature (the experimental data are from the NIST Webbook [23]). It was observed that the ionization energy of radical (IE_0) follows a similar pattern for each class of radicals (primary, secondary, tertiary, aryl, cycloalkane and vinyl).

Ionization energy has positive values because energy is always required to remove an electron. The ionization energy is

Table 3
Average absolute deviations for estimation of free radical enthalpies (kcal mol^{-1}) and correlation coefficients for the Mopac PM3 method

Radical	Mopac PM3	Mopac PM3-FC	Mopac PM3 correlated			
			AAD[a]	*a*	*b*	R^2
Primary	10.9900	0.7900	0.7961	0.9507	12.0930	0.9940
Secondary	16.8250	0.4000	0.3924	0.9618	17.0030	0.9989
Tertiary	17.5667	0.4667	3.6058	0.8215	19.3220	0.9993
Alken-α-yl	4.2182	2.6000	7.4469	0.9934	7.0417	0.9931
Cycloalkyl	16.6000	2.8250	2.0975	0.8435	20.2660	0.9840
Aryalk-α-yl	2.1000	0.4333	0.3716	0.7511	9.6657	0.9964

[a] AAD: average absolute deviation.

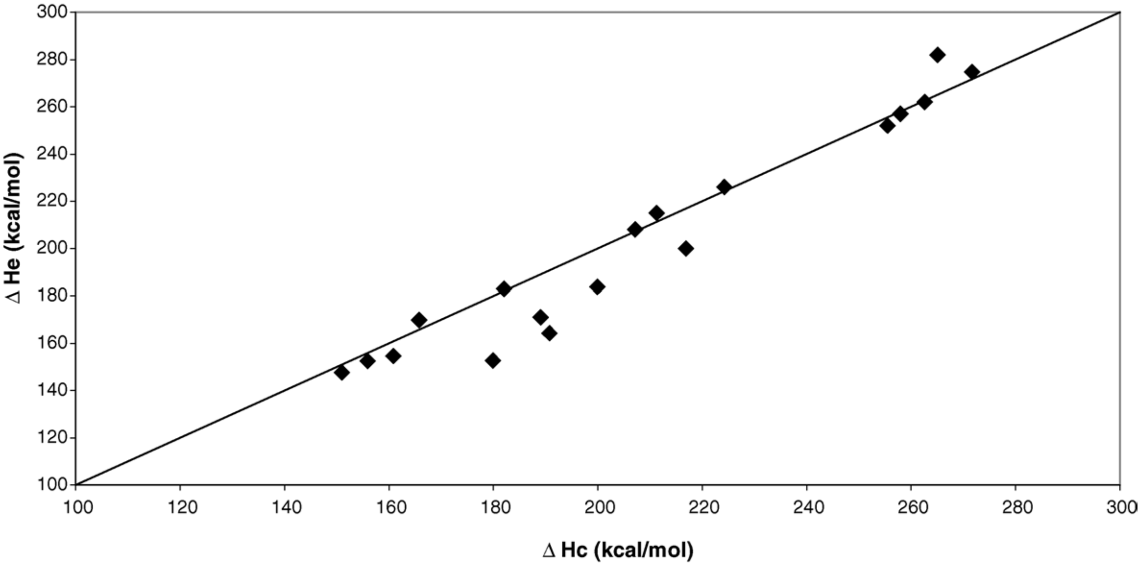

Fig. 9. Enthalpy of formation of carbocations at 298 K (kcal mol^{-1}).

lower when: (i) there is more shielding; (ii) the electron to be removed is spin paired (therefore there is repulsion); (iii) the electron is far from 'center of force'; (iv) there is more shielding from inner orbitals. Ionization energy increases when the charges are evenly distributed in the radical, the radical being more stable. This means that the ionization energy of radicals can be ordered, in a simplified view, by symmetry of charge distribution and level of shielding. The symmetry of charge distribution was considered to be similar in each class of the radicals: open chain hydrocarbons (alkyl, alken and alkyn), cycloalkan, aryl, etc. The shielding effect depends on the approximate location of full charge—primary, secondary and tertiary carbocations. Others correlations should be taken into account, such as the number of carbon atoms and particulars details of the bonding configuration.

Although in each class cited above, the ionization energy varies little except for small radicals. In the smaller ions the structure may be non-traditional. For example, the primary carbocations, i.e., species with the full positive charge localized in a primary carbon, species like CH_3^+ are not formed as intermediates in chemical reactions, and not even in the gas phase in an ion cyclotron resonance spectrometer [24]. In this work, we omitted small radicals with ionization energies above 8 eV.

The estimated average ionization energies of primary, secondary, tertiary, aryl primary, cycloalkane and of vinyl radicals, studied in this work, are $IE_0 = 183.5$, 166, 153.9, 162.6, 167.8 and 191 kcal mol^{-1}, respectively. Then, the enthalpy of formation of carbocations can be estimated as:

$$\Delta H_f^0(R^+) = \Delta H_f^{Benson}(R^\bullet) + IE_0 \quad (6a)$$

or

$$\Delta H_f^0(R^+) = \Delta H_f^{PM3}(R^\bullet) + IE_0 \quad (6b)$$

There are many methods that allow the experimental measurements of the standard enthalpies of formation of carbocations species. Actually, the most important of them are based in spectroscopy methodology such as high-pressure mass spectrometry (HPMS) and Fourier transform ion resonance spectroscopy (FT ICR) [25,26]. The quantitative ranking of stabilities can be obtained directly through FT ICR or indirectly, based on a ''dissociative proton attachment process'' (DPA) [26].

Although a variety of methodologies exist, there are only few experimental values directly determined for standard enthalpy of formation of carbocations. The calculated results for the carbocations, using modified Benson's method (Eq. (6a)), are compared with experimental values from literature as shown in Fig. 9. Estimated results agree qualitatively with values from literature and the absolute average deviation is 8.6 kcal mol^{-1}.

The correlation procedure to establish the location of full charge (i.e., primary, secondary and tertiary carbocations) and structural classification (i.e., alkane, cycloalkane, vinyl, aryl, etc.) cannot be directly adopted for carbocations as, actually, there are few evaluated experimental data.

4. Conclusions

The analysis of the results leads to following conclusions: The Benson's group contribution method provides accurate standard enthalpy of formation estimates for hydrocarbon molecules and comparable results to that of computationally intensive molecular simulation method (PM3) for free radicals. As proposed in this work, the standard enthalpies of formation can be estimated more accurately from a linear correlation of readily available experimental data with corresponding values calculated using Benson's or simple PM3 molecular simulation methods.

Based on the previous free radical enthalpy estimation and the estimated average ionization energy based on charge location and molecule structure, a simple method (Eq. (6a) and/or (6b)) is proposed for estimating approximately the enthalpies of formation of carbocations.

The present adaptation of Benson's method can be readily incorporated into a simulation software for hydroprocessing. In the present methodology, the Benson's method is used for representing functional structures of substances, radicals as well as carbocations. The estimated properties can also help in determining reaction pathways, estimating kinetic constants, chemical equilibrium conditions and energy balances.

Acknowledgements

The authors gratefully acknowledge the scholarship given by CNPq to K. Rajagopal (Bolsa de Produtividade) and to E. Moreno (Bolsa DTI). The financial support of CNPq/CTPETRO through the project "Caracterização Físico—Química de Frações Pesadas de Petróleo e Óleos Pesados", Process 502156/2003-1 and of CENPES/PETROBRAS is acknowledged. The authors also thank Dr. Ian Hovell for final revision of the text.

Appendix A. Experimental enthalpies of free radicals and carbocations

The standard enthalpy of formation of free radicals can be experimentally determined by one of three methods [22,25]: photoionization mass spectrometry (Method 1), negative ion cycles forming carbocations in hyperacid media as idealized by Olah and Arnett (Method 2) and by radical kinetics (Method 3). The energetics of experimental measurements of each method can be summarized by elementary steps as described below.

A.1. Method 1—photoionization mass spectrometry (PIMS)

$$\mathrm{RH} + h\nu \rightarrow \mathrm{R}^{+} + \mathrm{H}^{\bullet} + \mathrm{e}^{-} \quad \mathrm{AE}_{\mathrm{thresh}}(\mathrm{R}^{+}, \mathrm{RH}) \tag{A.1}$$

$$\mathrm{R}^{+} + \mathrm{e}^{-} \rightarrow \mathrm{R}^{\bullet} + h\nu \quad -\mathrm{IE}_0(\mathrm{R}^{\bullet}) \tag{A.2}$$

Summing (A.1) and (A.2),

$$\mathrm{RH} \rightarrow \mathrm{R}^{\bullet} + \mathrm{H}^{\bullet} \quad -\mathrm{DH}_0(\mathrm{RH}) \tag{A.3}$$

The bond energy $\mathrm{DH}_0(\mathrm{RH})$ or the enthalpy of reaction at 0 K, $\Delta_{\mathrm{rxn}}H_0$(A.3) is determined as:

$$\Delta_{\mathrm{rxn}}H_0(\mathrm{A.3}) \equiv -\mathrm{DH}_0(\mathrm{RH}) = \mathrm{AE}_{\mathrm{thresh}}(\mathrm{R}^{+}, \mathrm{RH}) - \mathrm{IE}_0(\mathrm{R}^{\bullet}) \tag{A.4}$$

where $\mathrm{AE}_{\mathrm{thresh}}(\mathrm{R}^{+}, \mathrm{RH})$ is appearance energy threshold and $\mathrm{IE}_0(\mathrm{R}^{\bullet})$ is the ionization energy of radical R.

A.2. Method 2—acidity/electron affinity cycle

$$\mathrm{RH} \rightarrow \mathrm{R}^{-} + \mathrm{H}^{+} \quad \Delta_{\mathrm{acid}}H_{298}(\mathrm{R{-}H}) \tag{A.5}$$

$$\mathrm{R}^{-} + h\nu \rightarrow \mathrm{R}^{\bullet} + \mathrm{e}^{-} \quad \mathrm{EA}_0(\mathrm{R}^{\bullet}) \tag{A.6}$$

$$\mathrm{H}^{+} + \mathrm{e}^{-} \rightarrow \mathrm{H}^{\bullet} + h\nu \quad -\mathrm{IE}_0(\mathrm{H}^{\bullet}) \tag{A.7}$$

Adding reactions (A.5) to (A.7) gives again the homolytic bond enthalpy in Eq. (A.3).

$$\mathrm{RH} \rightarrow \mathrm{R}^{\bullet} + \mathrm{H}^{\bullet} \quad -\mathrm{DH}_0(\mathrm{RH}) \tag{A.3}$$

And the corresponding enthalpy relation is:

$$\begin{aligned}\Delta_{\mathrm{rxn}}H_0(\mathrm{A.3}) &\equiv -\mathrm{DH}_0(\mathrm{RH}) \\ &= \Delta_{\mathrm{acid}}H_{298}(\mathrm{A.5}) + \mathrm{EA}_0(\mathrm{R}^{\bullet}) - \mathrm{IE}_0(\mathrm{H}^{\bullet}) \\ &\quad + [\text{thermal corrections}]\end{aligned} \tag{A.8}$$

where $\Delta_{\mathrm{acid}}H_{298}$ is the heterolytic bond enthalpy and in this case also known as enthalpy of deprotonation and EA_0 is the electron affinity. In Eq. (A.8), the value of thermal corrections $\int \Delta_{\mathrm{rxn}}C_{\mathrm{p}}\,\mathrm{d}T$ is generally less than 0.3 kcal mol^{-1}.

A.3. Method 3—radical kinetics

$$\mathrm{RH} + \mathrm{X}^{\bullet} \rightarrow \mathrm{R}^{\bullet} + \mathrm{HX} \quad \Delta_{\mathrm{rxn}}H_{298} \tag{A.9}$$

$$\mathrm{HX} \rightarrow \mathrm{H}^{\bullet} + \mathrm{X}^{\bullet} \quad -\Delta_{\mathrm{f}}H_{298}(\mathrm{HX}) \tag{A.10}$$

$$\mathrm{RH} \rightarrow \mathrm{R}^{\bullet} + \mathrm{H}^{\bullet} \quad -\mathrm{DH}_0(\mathrm{RH}) \tag{A.3}$$

And the corresponding enthalpy relation is:

$$\begin{aligned}\Delta_{\mathrm{rxn}}H_0(\mathrm{A.3}) &\equiv -\mathrm{DH}_0(\mathrm{RH}) \\ &= \Delta_{\mathrm{rxn}}H_{298}(\mathrm{A.7}) - \Delta_{\mathrm{f}}H_{298}(\mathrm{HX}) + [\text{thermal corrections}]\end{aligned} \tag{A.11}$$

Now we can obtain the experimental enthalpy of formation of radical $\mathrm{R}^{\bullet}$ directly from reaction (A.3) utilizing the enthalpy of formation of the molecule RH, $\Delta_{\mathrm{f}}\mathrm{H}_0(\mathrm{RH})$, and the value of $\Delta_{\mathrm{rxn}}\mathrm{H}_0$(A.3) obtained from relation (A.4), (A.8) or (A.11):

$$\Delta_{\mathrm{f}}H_{298}(\mathrm{R}^{\bullet}) = \Delta_{\mathrm{rxn}}H_0(\mathrm{A.3}) - \Delta_{\mathrm{f}}H_0(\mathrm{RH}) \tag{A.12}$$

The experimental values are available in NIST Chemistry Webbook [23] and from compilations and reviews in literature [25,26].

References

[1] H. Seki, F. Kumata, Energy Fuels 14 (2000) 980.
[2] W.R.A.M. Robinson, J.A.R. van Veen, V.H.J. de Beer, R.A. van Santen, Fuel Process. Technol. 61 (1999) 89.
[3] J.G. Speight, in: Proceedings of the International Symposium on Advances in Hydroprocessing of Oil Fractions (ISAHOF), Mexico, 2004.
[4] D. Salazar-Sotelo, R. Maya-Yescas, E. Mariaca-Domínguez, S. Rodríguez-Salomón, M. Aguilera-López, Catal. Today 98 (2004) 273.
[5] T.L.M. Maesen, S. Calero, M. Schenk, B. Smit, J. Catal. 221 (2004) 241.
[6] L. Fan, T. Watanabe, K. Fujimoto, Stud. Surf. Sci. Catal. 119 (1998) 581.
[7] C.S. Laxmi Narasimhan, J.W. Thybaut, G.B. Marin, J.F. Denayer, G.V. Baron, J.A. Martens, P.A. Jacobs, Chem. Eng. Sci. 59 (2004) 4765.
[8] E.C. Sanford, Ind. Eng. Chem. Res. 33 (1994) 109.
[9] M.L. Poutsma, J. Anal. Appl. Pyrol. 54 (2000) 5.
[10] B.A. Watson, M.T. Klein, R.H. Harding, Appl. Catal. A 160 (1997) 13.
[11] D.M. Fake, A. Nigam, M.T. Klein, Appl. Catal. A 160 (1997) 191.
[12] K. Basak, M. Sau, U. Manna, R.M. Verma, Catal. Today 98 (2004) 253.

[13] A. Westerberg, Process Flow Sheeting, first ed., Cambridge University Press, 1978 (Chapter 1).

[14] L.D.T. Câmara, K. Rajagopal, D.A.G. Aranda, Stud. Surf. Sci. Catal. 139 (2001) 61.

[15] K. Rajagopal, V. Ahon, M.A. Sugaya, in: Proceedings of FOCAPO 2003 Foundations of Computer-Aided Process Operations, Coral Cables, Florida, 2003.

[16] L.D.T. Câmara, H.S. Cerqueira, D.A.G. Aranda, K. Rajagopal, Catal. Today 98 (2004) 309.

[17] S.W. Benson, Thermochemical Kinetics, second ed., Wiley and Sons, 1976.

[18] K.G. Joback, R.C. Reid, Chem. Eng. Commun. 57 (1987) 233.

[19] TITAN Tutorial and User's Guide (Titan Manual), Wavefunction© 1999, Schrödinger, Inc.

[20] H.R. Perry, D.W. Green, Perry's Chemical Engineers Handbook, 7th ed., Sec. 3, McGraw-Hill, New York, 1997.

[21] X. Ma, H.H. Schoebert, J. Phys. Chem. A 104 (2000) 1064.

[22] J. Berkowitz, G.B. Ellison, D. Gutman, J. Phys. Chem. 98 (1994) 2744.

[23] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, Ion energetics data, in: P.J. Linstrom, W.G. Mallard (Eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, MD 20899, March 2003, http://webbook.nist.gov.

[24] http://chemistry.umeche.maine.edu/CHY556/carbocat.html, Department of Chemistry, University of Maine, USA (accessed on March 2005).

[25] K.M. Ervin, Chem. Rev. 101 (2001) 391.

[26] J.-L.M. Abboud, I. Alkorta, J.Z. Dávalos, P. Müller, E. Quintanilla, Adv. Phys. Org. Chem. 37 (2002) 57.