6524 *J. Phys. Chem. A* **2009,** *113,* 6524–6530

Energetics of *tert*-Butoxyl Addition Reaction to Norbornadiene: A Method for Estimating the π-Bond Strength of a Carbon−Carbon Double Bond

Paulo M. Nunes,*,† Sílvia G. Estácio,†,‡ Gustavo T. Lopes,† Filipe Agapito,†,‡ Rui C. Santos,† Benedito J. Costa Cabral,‡ Rui M. Borges dos Santos,†,§,∥ and José A. Martinho Simões*,†,§

Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal, Grupo de Física Matemática da Universidade de Lisboa, Av. Professor Gama Pinto, 2, 1649-003 Lisboa, Portugal, Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. da República, 2780-157 Oeiras, Portugal, and Institute for Biotechnology and Bioengineering, Centro de Biomedicina Molecular e Estrutural, Universidade do Algarve, Campus de Gambelas, 8005-139 Faro, Portugal

Received: January 5, 2009; Revised Manuscript Received: March 19, 2009

The energetics of *tert*-butoxyl radical addition reaction to norbornadiene was investigated by time-resolved photoacoustic calorimetry (TR-PAC). The result, together with the C−O bond dissociation enthalpy (BDE) in the addition product, allowed us to calculate the π-bond dissociation enthalpy in norbornadiene. Quantum chemistry (QC) methods were also used to obtain several enthalpies of reaction of the addition of oxygen-centered radicals to alkenes. The π-bond dissociation enthalpies in these molecules were calculated by a procedure similar to that used in the case of norbornadiene and were compared with the π-BDE values obtained by the method proposed by Benson. These two different approaches yield similar values for the π-BDEs in alkenes, indicating that the addition method proposed in the present study is a valid way to derive that quantity. The influence of strain in the π-BDEs of cyclic alkenes was investigated and allowed us to justify the difference between the π-BDE in norbornene and norbornadiene. Finally, the thermochemistry of the addition and abstraction reactions involving these two molecules and *tert*-butoxyl radical was analyzed.

Introduction

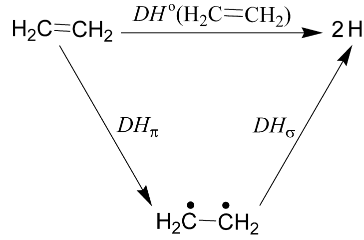
The addition of oxygen-centered radicals to carbon−carbon double bonds is an important step in mechanistic studies involving lipid peroxidation processes[1] and the tropospheric decomposition of terpenes.[2] Yet, to the best of our knowledge, the corresponding enthalpy of reaction has not been experimentally determined. An additional interest of this value is that it allows us to estimate a fundamental chemical quantity: the bond dissociation enthalpy (BDE) of a π-bond (DH_π) in an alkene. This quantity can be identified with the process illustrated for ethylene in Scheme 1, where DH_σ is the bond dissociation enthalpy of the σ bond.

There are several approaches to separate DH_σ from DH_π in $DH°(H_2C{=}CH_2)$.[3] The commonly accepted ways to estimate DH_π are the Benson method[3,4] and the determination of the energy barrier of the cis−trans isomerization reaction of alkenes.[3] More recently, a reaction scheme has been proposed to derive DH_π in cyclic alkenes using theoretical calculations[5] but which essentially consists of an alternative way of presenting the Benson method.

When the addition of a radical to a double bond occurs, the π bond is destroyed. Therefore, the enthalpy of this reaction may be used to obtain experimental DH_π values for alkenes. The method is particularly useful when the cis−trans isomerization method is not accessible, as in the case of cyclic alkenes or bicyclic alkenes such as norbornadiene.

Although the *tert*-butoxyl radical has a marked tendency to abstract allylic hydrogens,[6] the photolysis of di-*tert*-butylperoxide in the presence of norbornadiene generates a single product resulting from the addition of the *tert*-butoxyl radical to a double bond of norbornadiene.[7,8] This prompted us to apply this scheme to obtain the enthalpy of addition of oxygen-centered radicals to alkenes and to test the alternative experimental method of obtaining DH_π.

SCHEME 1



Experimental Section

Materials. Benzene (Aldrich, HPLC grade, 99.9+%) was used without further purification. Norbornadiene (Aldrich, 98%) was fractionally distilled over activated alumina(I) under nitrogen and used immediately. Di-*tert*-butylperoxide was purified according to a literature procedure.[9] *ortho*-Hydroxybenzophenone was recrystallized twice from an ethanol−water mixture.

Photoacoustic Calorimetry. The basis of photoacoustic calorimetry,[10,11] our photoacoustic calorimeter setup,[12,13] and the experimental technique are described in detail elsewhere.[13,14] Briefly, argon-purged solutions in benzene with ca. 0.4 M di-*tert*-butylperoxide and 0.39 to 0.79 M of norbornadiene were flowed through a quartz flow cell (Hellma 174-QS) and photolyzed with pulses from a nitrogen laser (PTI PL 2300,

---

* Corresponding author. E-mail: jams@fc.ul.pt (J.A.M.S.).

† Universidade de Lisboa.

‡ Grupo de Física Matemática da Universidade de Lisboa.

§ Universidade Nova de Lisboa.

∥ Universidade do Algarve.

10.1021/jp900089t CCC: $40.75

SCHEME 2

$$t\text{-BuOOBu-}t\text{ (sln)} \xrightarrow{h\nu} 2\ t\text{-BuO}^\bullet\text{ (sln)} \qquad (1)$$

$$2\ C_7H_8\text{ (sln)} + 2\ t\text{-BuO}^\bullet\text{ (sln)} \longrightarrow 2\ {}^\bullet C_7H_8O\text{-}t\text{-Bu (sln)} \qquad (2)$$

337.1 nm, pulse width 800 ps). The incident laser energy was varied by using neutral density filters (ca. 5−30 μJ/pulse at the cell). The photoacoustic signal was detected by a piezoelectric transducer (Panametrics V101, 0.5 MHz) in contact with the bottom of the cell, amplified (Panametrics 5662), and then collected using a digitizing oscilloscope (Tektronix 2430A). The signal-to-noise ratio was improved by averaging 32 acquisitions for each data point obtained at a given laser energy. The apparatus was calibrated by carrying out a photoacoustic run using an optically matched solution of *ortho*-hydroxybenzophenone (in the same mixtures but without the peroxide). The experiments were performed at 298 ± 1 K.

For each run (experiment or calibration), four data points were collected, corresponding to four different laser intensities obtained using the neutral density filters. The resulting waveforms from each data point were recorded for subsequent mathematical analysis, affording two waveforms for each point: sample and calibration. For each laser energy, the analysis involved first the normalization of both waveforms and then their deconvolution using the software Sound Analysis by Quantum Nortwest.[15] This procedure affords the observed fraction of photon energy released as heat, $\phi_{\mathrm{obs,i}}$ (related to the enthalpy), and the lifetimes, τ_i (related to the rate constant), for each process.

Theoretical Calculations. Different theoretical methods, including the complete basis-set composite schemes CBS-Q and CBS-QB3[16−18] were applied to determine the enthalpy of the addition reaction of the methoxyl radical to ethylene in the gas phase. (See eq 4, below.) Further calculations were based on a dual (D,T) scheme to complete basis set extrapolation of CCSD(T) energies relying on cc-pVDZ and cc-pVTZ calculations proposed by Truhlar.[19−22] The gas-phase C−H BDEs of norbornene were calculated using the CBS-QB3 scheme. Initially, optimized geometries and frequencies were determined at the B3LYP/cc-pVTZ level. The choice of this approach was oriented by previous investigations, indicating that it is adequate for a reliable prediction of both closed-shell and open-shell structures.[23] Thermal corrections to 298.15 K were based on B3LYP/cc-pVTZ unscaled frequencies. All of the calculations were carried out with the Gaussian 03 program.[24]

Results and Discussion

The sequential reactions presented in Scheme 2 were used in our TR-PAC experiments. The photolysis of di-*tert*-butylperoxide in benzene solution produces a pair of *tert*-butoxyl radicals (reaction 1). Each *tert*-butoxyl radical then reacts with a norbornadiene (C_7H_8) molecule, also present in solution (reaction 2).

The deconvolution analysis of the photoacoustic waves revealed the existence of three sequential steps. The first two are consistent with the reactions presented in Scheme 2: the lifetime of the first step corresponds to a prompt process (faster than the transducer response), and from $\phi_{\mathrm{obs,1}}$, an enthalpy value consistent with this homolysis reaction is derived;[14] from the lifetime obtained for step 2, τ_2, the rate constant (k_2) is estimated to be 2×10^6 M^{-1} s^{-1}, which is in good agreement with a reported laser flash photolysis value for the addition of the *tert*-butoxyl radical to norbornadiene, 3.22×10^6 M^{-1} s^{-1}.[7] The third process is much slower, with $\tau_3 \approx 3$ to 4 μs, independent from the concentration of norbornadiene. A possible candidate for this unimolecular step is the norbornenyl−nortricyclyl radical rearrangement.[8]

SCHEME 3

$$\begin{tikzcd}
{}^\bullet CH_2CH_2OMe \arrow[r, "E_1(C\text{–}O)"] \arrow[dr, "DH_1^o(C\text{–}O)"'] & MeO^* + C_2H_4^* \arrow[d, "ER_1"] \arrow[d, phantom, shift left=8ex, "\downarrow ER_2 = -DH_\pi"] \\
 & MeO^\bullet + C_2H_4
\end{tikzcd}$$

Only reaction 2 of Scheme 2 is important in the present study. The enthalpy of this reaction was derived from eq 3, where $\Delta_{\mathrm{obs}}H_2$ corresponds to the observed enthalpy change and is calculated by multiplying $E_m = N_A h\nu$ (the molar photon energy) by $\phi_{\mathrm{obs,2}}$. Φ_r is the quantum yield for the photolysis of di-*tert*-butylperoxide.

$$\Delta_r H_2 = \frac{-\Delta_{\mathrm{obs}}H_2}{\Phi_r} + \frac{\Delta_r V_2}{\chi} \qquad (3)$$

Because of the differences between the partial molar volumes of the reactants and products, a correction term is needed in eq 3,[25] which includes the reaction volume change, $\Delta_r V_2$, and the adiabatic expansion coefficient of the solution, χ, which is considered to be equal to the solvent because the solutions are dilute. The volume change of reaction 2 in Scheme 2 is caused by the contraction when the adduct ${}^\bullet C_7H_8O{-}t\text{-Bu}$ is formed from the two reactants. The typical value for contraction due to covalent bond formation is −10 mL mol^{-1}.[26,27] Using our experimental value for $\Delta_{\mathrm{obs}}H_2 = 154.2 \pm 7.5$ kJ mol^{-1}, the quantum yield for the photolysis of di-*tert*-butylperoxide in benzene, $\Phi_r = 0.83$,[28] the above estimate for the reaction volume change, $\Delta_r V_2 = -10$ mL mol^{-1}, and the adiabatic expansion coefficient of benzene, $\chi = 0.799$ mL kJ^{-1},[29] $\Delta_r H_2 = -198.3 \pm 9.0$ kJ mol^{-1} is derived.

To understand how this $\Delta_r H_2$ value can be used to derive the BDE of the π-bond in norbornadiene, we shall apply a similar scheme in a simpler case: the addition of a methoxyl radical to ethylene, reaction 4.

$$C_2H_4(g) + MeO^\bullet(g) \rightarrow {}^\bullet CH_2CH_2OMe(g) \qquad (4)$$

Scheme 3 relates the addition reaction 4 to DH_π in ethylene. In this scheme, the term E_1(C−O) is a "bond snap enthalpy", that is, the enthalpy associated with the bond cleavage process where the resulting fragments retain the same structure as that in the original molecule. As a result, we obtain the unrelaxed methoxyl radical MeO* and the unrelaxed $C_2H_4^*$ (which corresponds to the biradical $H_2C^\bullet{-}{}^\bullet CH_2$). This process is then followed by a relaxation of the fragments to their ground states. ER_2, the enthalpy associated with the relaxation of the radical $C_2H_4^*$ to ethylene, can be identified as the symmetrical of the π-BDE, that is, $ER_2 = -DH_\pi$. Equation 5 was derived from Scheme 3.

$$\Delta_r H_4^o = -DH_1^o(C{-}O) = -E_1(C{-}O) + DH_\pi - ER_1 \qquad (5)$$

To estimate E_1(C−O) let us consider Scheme 4, which involves the cleavage of the C−O bond in C_2H_5OMe. It is reasonable to assume that $E_1(C{-}O) \approx E_2(C{-}O)$ because the

SCHEME 4

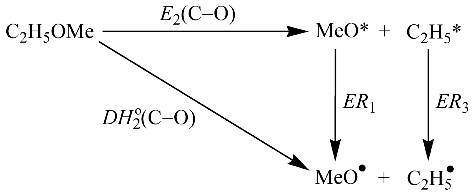


TABLE 1: π-Bond Dissociation Enthalpy in Several Alkenes, DH_π, Derived from Equation 8[a]

		$\Delta_rH^o_{add}$			
alkene	radical	CCSD(T)	CBS-Q	CBS-QB3	DH_π[b]
ethylene	MeO$^\bullet$	−83.3	−83.0	−82.3	276.3[c]
	t-BuO$^\bullet$		−78.4	−78.5	271.0[d]
trans-2-butene	MeO$^\bullet$		−86.2	−84.3	278.5[e]
cis-2-butene	MeO$^\bullet$		−88.7	−84.5	278.3[e]
norbornadiene	MeO$^\bullet$		−134.9	−129.8	226.5[f]
norbornene	MeO$^\bullet$			−111.5	244.8[f]

[a] Enthalpies of radical addition to the C=C bond, $\Delta_rH^o_{add}$ were estimated by using different theoretical methods. All values in kJ mol^{-1}. [b] Values calculated with the CBS-QB3 results. [c] Obtained using $DH^o(C-OR) = DH^o(C_2H_5-OMe) = 358.6 \pm 2.8$ kJ mol^{-1}. [d] $DH^o(C-OR) = DH^o(C_2H_5-O\text{-}t\text{-}Bu) = 349.5 \pm 3.9$ kJ mol^{-1}. [e] $DH^o(C-OR) = DH^o(i\text{-}Pr-OMe) = 362.8 \pm 2.9$ kJ mol^{-1}. [f] $DH^o(C-OR) = DH^o(t\text{-}Bu-OMe) = 356.3 \pm 3.0$ kJ mol^{-1}.

same type of bond is cleaved in C_2H_5OMe and in $^\bullet C_2H_4OMe$ radical. This assumption and Scheme 4 lead to eq 6.

$$E_1(C-O) \approx E_2(C-O) = DH_2^o(C-O) - ER_1 - ER_3 \quad (6)$$

By replacing $E_1(C-O)$ in eq 5 and assuming that the relaxation enthalpy of the ethyl radical is small, that is, $ER_3 \approx 0$, we obtain eq 7.

$$\Delta_rH_4^o = DH_\pi - DH_2^o(C-O) \quad (7)$$

The general form of our method is given by eq 8, where $\Delta_rH^o_{add}$ is the enthalpy of the addition of the $^\bullet$OR radical and $DH^o(C-OR)$ is the C−O BDE in the corresponding ether.

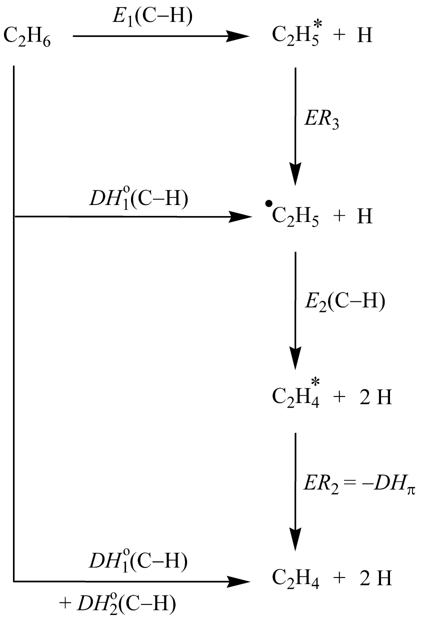
$$DH_\pi = \Delta_rH^o_{add} + DH^o(C-OR) \quad (8)$$

The CBS-Q, CBS-QB3, and CCSD(T) methods afforded the following values for $\Delta_rH^o_{add}$ which agree within 1 kJ mol^{-1} (Table 1): −83.0 kJ mol^{-1} (CBS-Q), −82.3 kJ mol^{-1} (CBS-QB3), and −83.0 kJ mol^{-1} (CCSD(T)). Taking $DH_2^o(C-OR) = DH^o(C_2H_5-OMe) = 358.6 \pm 2.8$ kJ mol^{-1} (derived from literature data),[30−32] the π-BDE in ethylene, $DH_\pi = 276$ kJ mol^{-1}, is obtained from eq 8. This result may be compared with the value calculated using the method proposed by Benson, which is simply the difference between the C−H BDEs in ethane and ethyl radical, $DH_1^o(C-H)$ and $DH_2^o(C-H)$, respectively (eq 9).

$$DH_\pi = DH_1^o(C-H) - DH_2^o(C-H) \quad (9)$$

Using literature data,[31,33,34] eq 9 leads to $DH_\pi = 274 \pm 2$ kJ mol^{-1}, which is in excellent agreement with the result from the addition method and also close to the value obtained from the kinetics of the cis−trans isomerization in $C_2D_2H_2$, $DH_\pi = 266$ kJ mol^{-1}.[3,35] The agreement suggests that the Benson approach and our addition reaction scheme are equivalent methods for estimating the π-BDE. To understand this conclusion, let us analyze the Benson method in detail by considering Scheme 5.

SCHEME 5



As explained in the previous schemes, $E_1(C-H)$ corresponds to the C−H bond snap enthalpy in ethane, followed by the enthalpy of relaxation of the ethyl radical, ER_3. The sum of these two steps is the C−H BDE in ethane, $DH_1^o(C-H)$. We can repeat this process for the ethyl radical and cleave a C−H bond vicinal to the radical center. In this case, the relevant quantities are $E_2(C-H)$, yielding the unrelaxed biradical $C_2H_4^*$, and ER_2, associated with the relaxation of this species to ethylene. Again, the sum of $E_2(C-H)$ and ER_2 is the C−H BDE in the ethyl radical, $DH_2^o(C-H)$. When the difference $DH_1^o(C-H) - DH_2^o(C-H)$ is calculated (Benson's approach), eq 10 is obtained.

$$DH_1^o(C-H) - DH_2^o(C-H) = E_1(C-H) - E_2(C-H) + ER_3 + DH_\pi \quad (10)$$

As stated before, it is reasonable to assume that $E_1(C-H) \approx E_2(C-H)$ because the same type of bond is being cleaved in ethane and in the ethyl radical. A second assumption is required to obtain Benson's relation (eq 9): the relaxation enthalpy of the ethyl radical should be very small, $ER_3 \approx 0$. Recall that similar assumptions were also made for our addition reaction scheme. It is therefore not surprising that the two approaches yield similar values for DH_π. Furthermore, because these two methods use different types of BDEs (C−O for the addition method and C−H for the Benson method) to derive DH_π in an alkene, they provide a good test of the thermodynamic consistency of the data used to calculate DH_π.

Having established the validity of the addition method for ethylene, we now turn to the DH_π value for norbornadiene, obtained from our TR-PAC data. Equation 8 applies to this situation, making $\Delta_rH^o_{add} = \Delta_rH_2^o/2$ and $DH^o(C-OR) = DH^o(C_7H_9-O\text{-}t\text{-}Bu)$. Although $\Delta_rH_2^o$ is a solution value, it is reasonable to assume that the correction due to solvation is negligible.[36]

Because $DH^o(C_7H_9-O\text{-}t\text{-}Bu)$ is not available, it must be estimated to obtain DH_π in norbornadiene. Values of $DH^o(R'-O\text{-}t\text{-}Bu)$ were calculated for several ethers (R′ = Me, Et, *i*-Pr, *t*-Bu) by using literature data.[30−32] It could be expected that $DH^o(C_7H_9-O\text{-}t\text{-}Bu)$ would be similar to $DH^o(i\text{-}Pr-O\text{-}t\text{-}Bu)$ because the C−O bond involves a secondary carbon atom

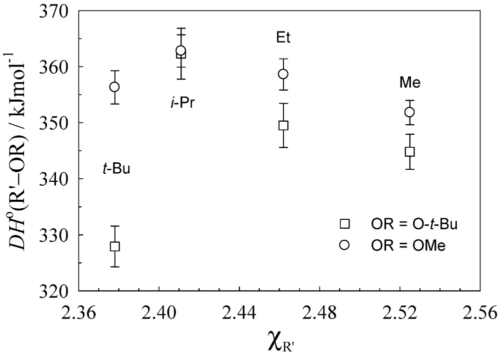


Figure 1. R′-OR bond dissociation enthalpies, $DH°$(R′−OR), for OR = OMe and O-*t*-Bu versus the electronegativity of R′ (Me, Et, *i*-Pr, *t*-Bu), $\chi_{R'}$.

in both cases. To test this hypothesis, the enthalpies of the addition reactions of *t*-BuO$^•$ to ethylene and MeO$^•$ to *cis*- and *trans*-2-butene were calculated with the CBS-QB3 composite scheme. By applying the appropriate $DH°$(C−OR) value in eq 8, viz. $DH°$(C_2H_5−O-*t*-Bu) = 349.5 ± 3.9 kJ mol^{-1} for the *t*-BuO$^•$ addition to ethylene and $DH°$(*i*-Pr−OMe) = 362.8 ± 2.9 kJ mol^{-1} in the case of the *cis*- or *trans*-2-butene, we derived DH_π values that are in good agreement with each other (Table 1), indicating that the addition method is valid as long as the correct value for $DH°$(C−OR) is chosen.

The estimate of $DH°$(C_7H_9−O-*t*-Bu) is, however, more complex. Data reported by Zavitsas et al. indicate that $DH°$(R′−OR) correlates linearly with Pauling electronegativity of R′ ($\chi_{R'}$) for a given R, in the absence of effects such as steric crowding, conjugation, or resonance.[37] Figure 1 shows the plot of $DH°$(R′−O-*t*-Bu) and $DH°$(R′−OMe) values against $\chi_{R'}$,[37] and it is noted that the value of $DH°$(R′−O-*t*-Bu) for R′ = *t*-Bu clearly deviates from the trend defined by R′ = Me, Et, and *i*-Pr. Indeed, using this trend, we would predict that $DH°$(*t*-Bu−O-*t*-Bu) should be some 40 kJ mol^{-1} higher than the experimental value (327.9 ± 3.6 kJ mol^{-1}). That extrapolated value for $DH°$(*t*-Bu−O-*t*-Bu) should reflect the inherent bonding ability between the two groups, free from steric crowding.[37] We shall assume that this steric effect is identical in *t*-Bu−O-*t*-Bu and C_7H_9−O-*t*-Bu. Using this assumption together with our experimental value of $\Delta_rH^o_{add} = (-198.3 \pm 9.0)/2$ kJ mol^{-1}, eq 8 yields $DH_\pi = 229 \pm 6$ kJ mol^{-1} in norbornadiene.

The addition reactions of the methoxyl radical to norbornadiene and norbornene are also presented in Table 1. As can be observed, the DH_π value derived for norbornadiene is in excellent agreement with our TR-PAC value (229 ± 6 kJ mol^{-1}). This supports the discussion regarding the choice of $DH°$ (C_7H_9−O-*t*-Bu); that is, the correct value for the C−O BDE must be estimated by considering not only the type of carbon (secondary or tertiary) but also the steric effect of R on the *t*-BuO−R BDE. The DH_π value in norbornene is ∼18 kJ mol^{-1} higher than the corresponding value in norbornadiene, indicating that the π-bond in the latter molecule is weaker than that in norbornene. This was a surprising result because the carbon−carbon double bond distances in these two molecules are similar (132.9 pm in norbornadiene and 133.4 pm in norbornene, obtained using B3LYP/cc-pVTZ optimized geometries). The Benson method (eq 9) can be applied to these two molecules using DH^o_1(C−H) = 413 ± 4 kJ mol^{-1} for norbornane[38] and DH^o_1(C−H) = 415 ± 4 kJ mol^{-1} for norbornene (obtained by CBS-QB3 calculations) and auxiliary thermochemical data from the literature.[31,34,39] Using this method, we obtain $DH_\pi = 253 \pm 8$ kJ mol^{-1} for norbornene and $DH_\pi = 231 \pm 7$ kJ mol^{-1} for norbornadiene (Table 2). Therefore, the Benson method also predicts that the π-bond in norbornene should be the strongest (a 21 kJ mol^{-1} difference is calculated).

One way to rationalize the DH_π difference in norbornadiene and norbornene is to consider the strain in both molecules. The strain of a molecule can be quantified by the value of its strain energy (E_{str}), calculated as the difference between its enthalpy of formation and the enthalpy of formation of a hypothetical strain-free reference molecule (indicated by an asterisk).[40,41] Equation 11 illustrates this for the case of an alkene.

$$E_{str} = \Delta_fH^o(\text{alkene, g}) - \Delta_fH^o(\text{alkene*, g}) \qquad (11)$$

Δ_fH^o(alkene*, g) can be obtained by applying the extended Laidler terms tabulated by Leal.[42] The data used for determining E_{str} and the DH_π for several alkenes are presented in Table 2.

The plot of DH_π versus the E_{str} values from Table 2, presented in Figure 2, suggests that there is some influence of strain in the π-bond dissociation enthalpy. This may explain the difference in the DH_π values for norbornene and norbornadiene. It is also interesting to note that cyclobutene and cyclopropene are clear exceptions from the plot. These two molecules show a different behavior because in the case of cyclopropene, the molecule has a high strain enthalpy due to a significant angular strain, whereas cyclobutene has an unexpectedly strong π-bond dissociation enthalpy, in keeping with its lower strain enthalpy.[5]

The model proposed in this work to estimate DH_π of a double bond involves the relation of this parameter to the enthalpy of the addition reaction of *tert*-butoxyl to that bond, cf. eq 8. Therefore, DH_π provides a quantitative way to discuss the reactivity of alkenes, namely, addition versus abstraction reactions. As stated in the Introduction, the *tert*-butoxyl radical favors the allylic abstraction reactions in alkenes when several types of C−H bonds are present. (See Figure 3.)[6,7] However, the reactivity of *t*-BuO$^•$ toward norbornene or norbornadiene is completely different because the only observed product is the adduct resulting from its addition to a double bond in these alkenes.[7] Using the values obtained in the present work, we can discuss the thermodynamics of those two competing reactions and try to understand this drastic change of reactivity. The results are displayed in Table 3.

The enthalpies of the abstraction reactions, $\Delta_rH^o_{abst}$, were obtained with eq 12.

$$\Delta_rH^o_{abst} = DH^o(\text{C−H}) - DH^o(t\text{-BuO−H}) \qquad (12)$$

The allylic C−H BDE, $DH°$(C−H), was calculated by the CBS-QB3 method for norbornene to be $DH°$(C1−H) = 453.5 ± 4.0 kJ mol^{-1}. Because this value is very similar to the C1−H BDE in norbornane (449 ± 4 kJ mol^{-1}),[38] it was also assigned to the C1−H BDE in norbornadiene. In the other cyclic alkenes (Table 3), the allylic C−H BDEs were obtained from previous work.[41] The value for the O−H BDE in *tert*-butanol was taken to be $DH°$(*t*-BuO−H) = 444.9 ± 2.8 kJ mol^{-1}.[44]

In the abstraction reaction, two reacting molecules yield two product molecules, being reasonable to assume that $\Delta_rS^o_{abst} \approx 0$. Therefore, the standard Gibbs energy of the abstraction reaction is identified with the reaction enthalpy, $\Delta_rG^o_{abst} \approx \Delta_rH^o_{abst}$.

The enthalpies of the addition reaction were derived from eq 8, using the DH_π values calculated with the Benson method (Table 2) together with $DH°$(C−O-*t*-Bu) = 327.9 ± 3.6 kJ mol^{-1} for the addition of *t*-BuO$^•$ to norbornene and norbornadiene or $DH°$(C−O-*t*-Bu) = 362.3 ± 4.5 kJ mol^{-1} for the addition to other cycloalkenes (Table 1). Using literature data[45] and model reactions[46] (Scheme 6), we estimated $-T\Delta_rS^o_{add} \approx$

TABLE 2: Auxiliary Data Used to Determine E_{str} and DH_π for Several Alkenes[a]

alkene	DH_1°(C−H)	DH_2°(C−H)	$\Delta_f H^\circ$(alkane, g)[b]	$\Delta_f H^\circ$(alkene, g)[b]	$\Delta_f H^\circ$(alkene*, g)	E_{str}[c]	DH_π
ethylene	423.0 ± 1.7[d]	149.3 ± 1.7	−83.8 ± 0.3	52.5 ± 0.3	52.5	0.0	273.7 ± 2.4
norbornene	413.4 ± 4.0[e]	160.4 ± 6.4	−54.8 ± 4.6	82.6 ± 2.1[f]	4.8	77.8	252.6 ±7.6
norbornadiene	414.6 ± 4.0[g]	183.7 ± 5.3	82.6 ± 2.1[f]	245.3 ± 2.7[f]	117.6	127.7	231.3 ± 6.6
cyclopentene	403.0 ± 4.0[h]	143.4 ± 4.3	−76.4 ± 0.7	34.0 ± 1.4	11.1	22.9	259.6 ± 5.9
cyclohexene	414.6 ± 4.0[h]	139.8 ± 4.1	−123.3 ± 0.8	−4.9 ± 0.6	−9.7	4.8	274.8 ± 5.7
1,3-cyclopentadiene	404.8 ± 4.0[h]	131.5 ± 4.5	34.0 ± 1.4[i]	134.3 ± 1.5[i]	109.3	25.0	273.3 ± 6.0
1,4-cyclohexadiene	413.9 ± 4.0[h]	131.8 ± 4.1	−4.9 ± 0.6[i]	104.8 ± 0.6[f,i]	105.0	−0.2	282.1 ± 5.7
1,3-cyclohexadiene	413.9 ± 4.0[h]	131.6 ± 4.1	−4.9 ± 0.6[i]	104.6 ± 0.6[f,i]	88.6	16.0	282.3 ± 5.7
cyclobutene	418.8 ± 4.0[j]	146.2 ± 4.4	27.7 ± 1.1	156.7 ± 1.5	31.8	124.9	272.6 ± 6.0
cyclopropene	455.6 ± 4.0[j]	204.2 ± 4.7	53.3 ± 0.5	277.1 ± 2.5	52.5	224.6	251.5 ± 6.2

[a] DH_1°(C−H) is the C−H BDE in the corresponding alkane, DH_2°(C−H) is the C−H BDE in the corresponding radical obtained from auxiliary data (see note 34), $\Delta_f H^\circ$(alkane, g) is the enthalpy of formation of the alkane, $\Delta_f H^\circ$(alkene, g) is the enthalpy of formation of the alkene, $\Delta_f H^\circ$(alkene*, g) is the enthalpy of formation of a strain-free reference alkene (obtained using the Laidler terms in ref 42), E_{str} is the strain enthalpy obtained through eq 11, and DH_π is the π-bond dissociation enthalpy calculated using the Benson method, eq 9. All values in kJ mol^{-1}. [b] Ref 31 unless stated otherwise. [c] See ref 41. These values can also be compared with data reported by Rogers, D. W.; et al. *J. Phys. Chem. A* **2008**, *112*, 5734−5741 and references therein (values in kJ mol^{-1}): E_{str}(cyclopentene) = 25, E_{str}(cyclohexene) = 6.3, E_{str}(1,4-cyclohexadiene) = 4.2 ± 2.9, E_{str}(norbornene) = 85.4, E_{str}(norbornadiene) = 129. Following the procedures outlined in the same reference, one can calculate E_{str}(cyclobutene) = 125.5 and E_{str}(cyclopropene) = 225. [d] Ref 33. [e] Ref 38. [f] Selected from ref 39. [g] Calculated by CBS-QB3. [h] Ref 41. [i] In this case, "alkane" corresponds to alkene and "alkene" to diene. [j] Ref 43.

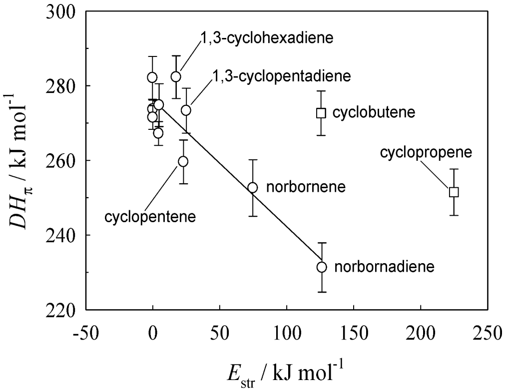


Figure 2. Plot of the π-bond dissociation enthalpy, DH_π, versus the strain enthalpy, E_{str}. Data from Table 2.

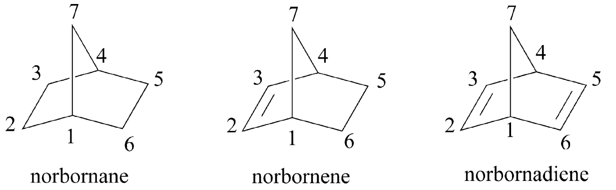


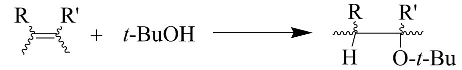
Figure 3. Norbornane, norbornene, and norbornadiene structures showing carbon atom numbering.

TABLE 3: Thermochemical Data for the Abstraction and Addition Reactions of *tert*-Butoxyl Radical with Cyclic Alkenes[a]

alkene	DH°(C1−H)	$\Delta_r H^\circ_{abst}$	$\Delta_r H^\circ_{add}$	$\Delta_r G^\circ_{add}$
norbornene	453.5 ± 4.0[c]	8.6 ± 4.9	−75.3 ± 8.4	−20.3 ± 9.3
norbornadiene	453.5 ± 4.0[d]	8.6 ± 4.9	−96.6 ± 7.5	−41.6 ± 8.5
cyclopentene	358.7 ± 4.0[e]	−86.2 ± 4.9	−102.7 ± 7.4	−47.7 ± 8.4
cyclohexene	357.9 ± 4.0[e]	−87.0 ± 4.9	−87.5 ± 7.3	−32.5 ± 8.3
1,3-cyclopentadiene	355.0 ± 8.0[f]	−89.9 ± 8.5	−89.0 ± 7.5	−34.0 ± 8.5

[a] DH°(C1−H) are allylic C1−H BDEs. All values in kJ mol^{-1}. [b] $\Delta_r G^\circ_{abst} \approx \Delta_r H^\circ_{abst}$ (see text). Refers to the abstraction reaction from C1. [c] This work, calculated by CBS-QB3. [d] Assumed to be equal to DH°(C1−H) in norbornene. [e] Ref 41. [f] Ref 13.

SCHEME 6



55 kJ mol^{-1} (T = 298.15 K) for the addition of a *tert*-butoxyl radical to a double bond.

As observed in Table 3, the abstraction reactions of the allylic hydrogens from norbornene and norbornadiene are thermodynamically unfavorable, whereas the addition reactions are exergonic. This is a direct result of very high allylic C−H BDEs and low π-BDEs in these molecules. However, the most probable site for abstraction in norbornene will be at the C5 rather than at C1. Because DH°(C5−H) = 413.4 ± 4.0 kJ mol^{-1} is lower than DH°(C1−H), $\Delta_r H^\circ_{abst}$ becomes exothermic (−32 ± 5 kJ mol^{-1}), and the addition and abstraction reactions now have similar $\Delta_r G^\circ$ values within the experimental uncertainties. The addition reaction must be kinetically more favorable, because it is the only one observed. This is in keeping with the rate constants of the reaction of *tert*-butoxyl radical with these molecules. In the case of norbornadiene, where only addition should be observed, the rate constant is $k_{add} = 3.2 \times 10^6$ M^{-1} s^{-1}. For norbornene, the same rate constant is $k_{add} = 1.1 \times 10^6$ M^{-1} s^{-1}, whereas the abstraction reaction (from C2 or C5) in norbornane has $k_{abst} = 5.8 \times 10^5$ M^{-1} s^{-1}.[7] Because DH°(C2−H) in norbornane[38] is similar to DH°(C5−H) in norbornene, it is expected that the abstraction reaction of C5−H in norbornene should have a rate constant $k_{abst} \approx 10^5$ M^{-1} s^{-1}. Although the kinetic data were obtained in benzene solution, a similar trend can be expected for the gas phase.

In the other cyclic alkenes (Table 3), viz. cyclopentene, cyclohexene, and 1,3-cyclopentadiene, we can conclude that the abstraction reactions will be the thermodynamically preferred pathway for the *tert*-butoxyl radical. Although in some cases the enthalpies of the abstraction and addition reactions are very similar, the entropic factor raises the standard Gibbs energy of the addition reactions, making them less exergonic. Previous studies of the reactions of the *tert*-butoxyl radical with cyclopentene, 1,3-cyclopentadiene,[7] and cyclohexene[47] support these conclusions.

Conclusions

A new way to evaluate the π-bond dissociation enthalpy of a double bond (DH_π), relying on the enthalpy of addition of a radical to that bond, leads to results that are in very good agreement with those obtained from an early procedure proposed by Benson and also with the so-called cis−trans isomerization reaction method. The addition approach is particularly useful in cases where the latter method cannot be applied to calculate DH_π, for example, cyclic alkenes. As shown in the discussion, the addition and the Benson methods are based on similar assumptions. However, special attention should be paid to choosing a suitable DH°(C−OR) for the addition model (required to derive DH_π). It was also noted that there is some dependence between DH_π and the strain of the alkene.

The relationship between the enthalpy of addition of *tert*-butoxyl to a double bond and its π-bond enthalpy prompted us to analyze the thermochemistry of the reactions of the *tert*-butoxyl radical toward cyclic alkenes. The preference for the addition reaction of the *tert*-butoxyl radical to norbornene and norbornadiene versus H-abstraction reaction was rationalized considering the low DH_π values and the abnormally strong "allylic" C−H BDE in these molecules (as a result of a highly strained geometry). In other cyclic alkenes, we have shown that the entropic factor disfavors the addition reaction versus the C−H allylic abstraction.

Note Added in Proof. As pointed out by a reviewer, the π-BDE values can also be obtained from available literature values of enthalpies of formation and of hydrogenation. For instance, the π-bond strength in (*E*)-2-butene gives the value for an unstrained 1,2-disubstituted alkene. It can be obtained by eq 9: $DH_\pi = DH_1^\circ(\mathrm{C{-}H}) - DH_2^\circ(\mathrm{C{-}H})$, where DH_1°(C−H) refers to the secondary C−H BDE in butane and DH_2°(C−H) refers to the $CH_3C^\bullet HCH(CH_3)$−H BDE. Using $DH_1^\circ(\mathrm{C{-}H}) = 410.9 \pm 2.1$ kJ mol^{-1} [30] and $DH_2^\circ(\mathrm{C{-}H}) = 139.4 \pm 2.4$ kJ mol^{-1} (derived using the enthalpies of formation of butane and (*E*)-2-butene given by Pedley),[31] we obtain $DH_\pi = 271.5$ kJ mol^{-1}.[30] Using the same values from Pedley's compilation, we calculated the enthalpy of hydrogenation, ΔH_{hyd}, of (*E*)-2-butene to be -114.3 kJ mol^{-1}. Now, the enthalpies of formation of norbornane and norbornene, -54.8 ± 4.6 kJ mol^{-1} and 82.6 ± 2.1 kJ mol^{-1}, respectively,[31,39] lead to $\Delta H_{\mathrm{hyd}}(\mathrm{norbornene}) = -137.4$ kJ mol^{-1}, that is 23.1 kJ mol^{-1} more exothermic than that of the unstrained (*E*)-2-butene. Therefore the π-BDE of norbornene is estimated to be $271.5 - 23.1 = 248.4$ kJ mol^{-1}, which is rather close to the values displayed in Tables 1 and 2, 244.8 and 252.6 kJ mol^{-1}, respectively. A similar exercise for the hydrogenation of one double bond in norbornadiene leads to an enthalpy of hydrogenation of -162.7 kJ mol^{-1} and to $DH_\pi =$ 223.1 kJ mol^{-1}, also close to the values in Tables 1 and 2, 226.5 and 231.3, respectively. This alternative method, suggested by the reviewer, not only confirms the DH_π values obtained by the two methods discussed above, but also implicitly assumes that there is a strong influence of strain in the π-BDE of cyclic hydrocarbons.

Acknowledgment. This work was supported by Fundação para a Ciência e a Tecnologia (FCT), Portugal (PTDC/QUI/65535/2006). P.M.N. and R.C.S. thank FCT for postdoctoral grants (SFRH/BPD/26677/2005 and SFRH/BPD/26610/2006, respectively), and S.G.E. and F.A. acknowledge Ph.D. grants (SFRH/BD/10200/2002 and SFRH/BD/22854/2005, respectively). We also acknowledge an excellent suggestion given by a reviewer, which originated the "Note Added in Proof" of the present article.

Supporting Information Available: Computed optimized geometries and total energies for radicals and parent compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Cheng, Z.; Li, Y. *Chem. Rev.* **2007**, *107*, 748–766.

(2) Peeters, J.; Boullart, W.; Pultau, V.; Vandenberk, S.; Vereecken, L. *J. Phys. Chem. A* **2007**, *111*, 1618–1631.

(3) Miller, S. I. *J. Chem. Educ.* **1978**, *55*, 778–780.

(4) Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 6750–6755.

(5) Bach, R. D.; Dmitrenko, O. *J. Am. Chem. Soc.* **2004**, *126*, 4444–4452.

(6) Small, R. D.; Scaiano, J. C.; Patterson, L. K. *Photochem. Photobiol.* **1979**, *29*, 49–51.

(7) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5106–5108.

(8) Wong, P. C.; Griller, D. *J. Org. Chem.* **1981**, *46*, 2327–2329.

(9) Diogo, H. P.; Minas da Piedade, M. E.; Martinho Simões, J. A.; Nagano, Y. *J. Chem. Thermodyn.* **1995**, *27*, 597–604.

(10) Peters, K. S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 294–302.

(11) Braslavsky, S. E.; Heibel, G. E. *Chem. Rev.* **1992**, *92*, 1381–1410.

(12) Borges dos Santos, R. M.; Lagoa, A. L. C.; Martinho Simões, J. A. *J. Chem. Thermodyn.* **1999**, *31*, 1483–1510.

(13) Nunes, P. M.; Agapito, F.; Costa Cabral, B. J.; Borges dos Santos, R. M.; Martinho Simões, J. A. *J. Phys. Chem. A* **2006**, *110*, 5130–5134.

(14) Correia, C. F.; Nunes, P. M.; Borges dos Santos, R. M.; Martinho Simões, J. A. *Thermochim. Acta* **2004**, *420*, 3–11.

(15) *Sound Analysis*, version 1.50D; Quantum Northwest: Spokane, WA, 1999.

(16) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A. *J. Chem. Phys.* **1996**, *104*, 2598–2619.

(17) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822–2827.

(18) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532–6542.

(19) Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 35.

(20) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968–5975.

(21) Krishnam, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244–4245.

(22) Truhlar, D. G. *Chem. Phys. Lett.* **1998**, *294*, 45–48.

(23) Byrd, E. F. C.; Sherrill, C. D.; Head-Gordon, M. *J. Phys. Chem. A* **2001**, *105*, 9736–9747.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford CT, 2004.

(25) Hung, R. R.; Grabowski, J. J. *J. Am. Chem. Soc.* **1992**, *114*, 351–353.

(26) le Noble, W. J.; Kelm, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 841–946.

(27) It should be noted that even if this estimate is wrong by 50%, the variation in the final value of DH_π calculated through eq 8 is only ca. 3 kJ mol^{-1}.

(28) Wayner, D. D. M.; Lusztyk, E.; Pagé, D.; Ingold, K. U.; Mulder, P.; Laarhoven, L. J. J.; Aldrich, H. S. *J. Am. Chem. Soc.* **1995**, *117*, 8737–8744.

(29) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986.

(30) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744–2765.

(31) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994; Vol. I.

(32) Ruscic, B.; Boggs, J. E.; Burcat, A.; Csaszar, A. G.; Demaison, J.; Janoschek, R.; Martin, J. M. L.; Morton, M. L.; Rossi, M. J.; Stanton, J. F.; Szalay, P. G.; Westmoreland, P. R.; Zabel, F.; Berces, T. *J. Phys. Chem. Ref. Data* **2005**, *34*, 573–656.

(33) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255–263.

(34) The C−H BDEs of alkanes, DH°_1(C−H), are easily found in the literature; DH°_2(C−H) values are usually calculated from the enthalpies of formation of the radical and the alkene. In the case under discussion, $DH^\circ_2(\mathrm{C-H}) = \Delta_f H^\circ(\mathrm{C_2H_4,g}) + \Delta_f H^\circ(\mathrm{H,g}) - \Delta_f H^\circ(\mathrm{C_2H_5^\bullet,g})$.

(35) Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315–323.

(36) $\Delta_r H^\circ_2$, (gas)/2 $= \Delta_r H^\circ_2(\mathrm{sln})/2 + \Delta_{sln} H^\circ(\mathrm{C_7H_9}) + \Delta_{sln} H^\circ(t\text{-BuO}^\bullet) - \Delta_{sln} H^\circ(\mathrm{C_7H_9{-}O}\text{-}t\text{-Bu})$ but the solvation terms in benzene should cancel out. As shown below, the DH_π value for norbornadiene obtained in the gas phase using the addition reaction of methoxyl radical (Table 1) and the DH_π derived using eq 8 are identical, suggesting that this assumption is correct.

(37) Matsunaga, N.; Rogers, D. W.; Zavitsas, A. A. *J. Org. Chem.* **2003**, *68*, 3158–3172.

(38) Nunes, P. M.; Estácio, S. G.; Lopes, G. T.; Costa Cabral, B. J.; Borges dos Santos, R. M.; Martinho Simões, J. A. *Org. Lett.* **2008**, *10*, 1613–1616.

(39) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. In *NIST Chemistry WebBook*; NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD, 2005. http://webbook.nist.gov.

(40) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, NY, 1970.

(41) Agapito, F.; Nunes, P. M.; Costa Cabral, B. J.; Borges dos Santos, R. M.; Martinho Simões, J. A. *J. Org. Chem.* **2008**, *73*, 6213–6223.

(42) Leal, J. P. *J. Phys. Chem. Ref. Data* **2006**, *35*, 55–76.

(43) Feng, Y.; Liu, L.; Wang, J.-T.; Zhao, S.-W.; Guo, Q.-X. *J. Org. Chem.* **2004**, *69*, 3129–3138.

(44) Ervin, K. M.; DeTuri, V. F. *J. Phys. Chem. A* **2002**, *106*, 9947–9956.

(45) Stull, D. R.; Westrum, Jr. , E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(46) Minas da Piedade, M. E.; Martinho Simões, J. A. *J. Organomet. Chem.* **1996**, *518*, 167–180.

(47) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393–6397.

JP900089T