A Hard−Soft Acid−Base and DFT Analysis of Singlet−Triplet Gaps and the Addition of Singlet Carbenes to Alkenes

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The electronic structures of sixteen carbenes and four alkenes calculated at the B3LYP/6-31G* level were used to carry out a hard−soft acid−base investigation of carbene singlet−triplet gaps and of the addition of carbenes to alkenes. The carbenes chosen include examples where the ground state varies from triplet to singlet state and examples that have been characterized as nucleophilic, electrophilic, or ambiphilic based on their reactivity with alkenes having varying electron demands. We confirmed that singlet−triplet gaps calculated by DFT methods with the B3LYP functional correlate well with experimentally known values of carbenes spanning over 70 kcal/mol. Correlations between electron-density-based parameters and singlet−triplet gaps, or with carbene−alkene reactivity, were analyzed to gain insight into the electronic structure of the carbenes and their acid−base tendencies. A good correlation was found between the singlet−triplet energy gap and the condensed softness for electrophilic attack at the triplet carbene carbon $[s_C^-(T)]$, which reflects the level of carbene stability upon electron donation. Trends in electron donation between carbenes and alkenes with different electrophilicities and nucleophilicities analyzed by the electronegativity equalization principle correlate well with Moss' reactivity indices. We also found that interaction energies calculated between alkenes and carbenes are most favorable with parameters that reflect mutual electron donation, reflecting the simultaneous acidity and basicity of carbenes and alkenes.

Introduction

The hard and soft acid−base principle (HSAB)[1] based on density functional theory (DFT)[2] represents an expanding theoretical approach that is based on the examination of electronic density changes as the primary source of energetic and structural information to analyze equilibrium and reactivity. In a simple but rapidly evolving approximation, it is expected that chemical reactions should reflect mutual electronic perturbations between prospective reactants and that useful chemical information should be contained within their ground states. In the ideal case scenario, reactivities, selectivities, and specificities would be predictable from (or correlated with) experimental electronic densities available from X-ray diffraction or atomic scale microscopy (i.e., AFM or STM). In practice, the analysis of electronic density properties can be carried out from electronic structures calculated with semiempirical and ab initio methods (Hartree−Fock and/or DFT).

One of the most intriguing aspects of the density functional approach comes from the suggestion that simple parameters obtained from experimental or calculated electronic affinities (*A*) and ionization potential (*I*) may yield reactivity tendencies with approximations that may be as useful as those obtained by a frontier molecular orbital (FMO)-based HOMO−LUMO analysis. One promising method of analysis entails the calculation of charge exchange (ΔN) and interaction energies (ΔE_{int}) between prospective reactants. In a DFT context, one may formulate a chemical problem in terms of a structure with *N* electrons that are subject to an external potential $v(\mathbf{r})$ which is due to the nuclei.[1] DFT parameters such as chemical potential (μ), hardness (η), and softness (*S*) respond to changes on the energy of the system and depend on the number of electrons (*N*) and the external potential $v(\mathbf{r})$. Several DFT parameters can be calculated for entire molecules, for localized regions, and at the atomic level, to give global, local, and condensed properties. The chemical potential (μ) is identified as the negative of the electronegativity (χ),[3] the hardness (η) is the change of chemical potential with respect the number of electrons,[4] and the softness is the inverse of the global hardness and is related to polarizability.[5] Recent DFT applications to organic reactions include Michael additions,[6] Diels−Alder reactions,[7] 1,3-dipolar cycloadditions,[8] and the S_N2 vs E2 selectivity.[9] The results obtained in those studies suggest the utility of the method to analyze

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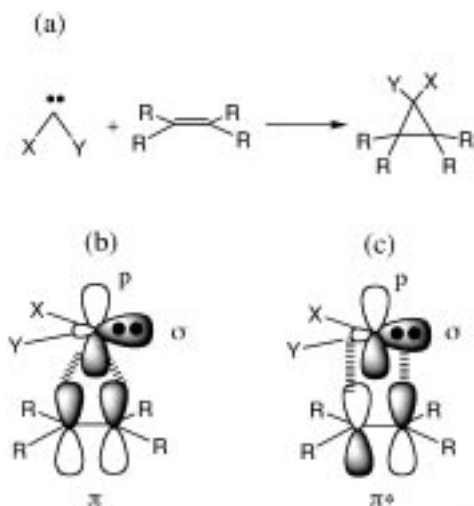
Scheme 1

the position of attack, the direction of electron transfer, the importance of electronic reorganization on the total electron density flow expected in the reaction, and the acid and base properties of the reactants.

As a test of this DFT methodology, we have analyzed some aspects of the electronic structure of simple carbenes and their addition reaction to olefins. Carbenes are among the most interesting organic species with singlet and triplet states that have energies and reactivities that depend sensitively on the nature of their substituents. Singlet carbenes react stereospecifically with alkenes in a reaction where the carbene carbon expands its number of valence electrons from six to eight (Scheme 1a). Although a net flow of electrons from the alkene to the carbene carbon would suggest that all carbenes should be considered electrophilic, Moss demonstrated in the late 1970s that some carbenes have strong nucleophilic tendencies.[10] An elegant FMO model based on orbital interactions and orbital energies successfully accounted for selectivity trends and predicted the existence of ambiphilic carbenes. Ambiphilic carbenes act as electrophiles toward electron-rich alkenes and as nucleophiles toward electron-poor alkenes. The dominant FMO interaction between electrophilic carbenes and alkenes and between nucleophilic carbenes and alkenes are shown in Scheme 1b and c, respectively. It was shown that the relative contributions of the FMO interactions shown in Scheme 1 depend strongly on the nature of the substituents R on the alkene and the substituents X and Y on the carbene carbon. For instance, dichlorocarbene and chloromethyl carbene react faster with electron-rich alkenes and have a predominant π(alkene)$-$p(carbene) interaction (Scheme 1b). In contrast, dimethoxy- and diaminocarbenes have a nucleophilic tendency and react faster with electron poor alkenes, presumably through a dominant HOMO$-$LUMO interaction between the complementary set of frontier orbitals in Scheme 1c: π*-(alkene)$-\sigma$(carbene).

The reaction between carbenes and alkenes can also be formulated in terms of acid$-$base interactions with carbenes and alkenes acting either as electron donors or electron acceptors. In this paper, we have explored this

point of view by analyzing the effect of substituents on the electron-donating and electron-accepting abilities of a set of carbenes and a set of olefins with different electronic demands. We have also analyzed DFT parameters that correlate with of the magnitude of the singlet$-$triplet gap and the nature of the most favorable electronic interactions between carbenes and alkenes.

Computational Methodology

The structures and energies of sixteen singlet and triple state carbenes with silyl, methyl, chloro, fluoro, hydroxy, methoxy, and phenyl substituents were calculated at the B3LYP/6-31G* level by means of GAUSSIAN94 (Table 1).[11] The structures and energies of the oxidized and reduced (cation and anion) species were calculated at the equilibrium geometry of the neutral for all of the carbenes included in the study. In agreement with recent reports with the B3LYP and other functionals,[12−16] excellent values were obtained for all experimentally known singlet$-$triplet energy gaps (ΔE_{ST}). A very close agreement was also found between the DFT values obtained here and those reported by Goddard et al. using a balanced GVB approach that was adjusted to fit experimental values.[17] For carbenes with more than one conformation, the ΔE_{ST} for the lowest energy conformers are reported.

Results and Discussion

DFT Analysis of Singlet$-$Triplet Gaps. Although the B3LYP values give singlet$-$triplet energy gaps systematically lower by 2 to 4 kcal/mol, the agreement with experimental ΔE_{ST} values spans over 70 kcal/mol with sylanyl and difluorocarbene at the two extremes. As shown in Figure 1, a good linear correlation was obtained between the singlet$-$triplet gaps and the Kohn$-$Sham orbitals HOMO$-$LUMO energy differences for the singlet carbenes.[18] There was also a good correlation between the Hartree$-$Fock orbitals HOMO$-$LUMO energy differences calculated by Houk et al. and our calculated singlet$-$triplet gaps.[10] However, a relation between the singlet$-$triplet gaps and the charge of the triplet carbene carbons found by Goddard et al. for silanyl and halo carbenes did not stand for our extended series with methoxy, hydroxy and phenyl carbenes.

In order to evaluate the effects of substituents on the electronic structure of the divalent carbon atom, and to explore how these changes affect the energy differences between the singlet and triplet state, the energies of the oxidized and reduced (cation and anion) carbenes at the

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Table 1. Singlet−Triplet Energy Gaps (kcal/mol) and DFT Parameters in Atomic Units (au) for the Singlet and Triplet (parentheses values) States of a Series of Carbenes Analyzed in this Study

carbene	$\Delta E_{ST}{}^a$	$\Delta E_{ST}{}^b$	$\Delta E_{ST}{}^c$	μ^d	η^e	S^f	$f_C{}^g$	f_C^{+h}	$f_C^{o\,i}$	s_C^-
HCSiH$_3$	−23.27		−19.08	−0.21	0.169	5.917	0.26	0.301	0.281	
				(−0.172)	(0.185)	(5.405)	(0.304)	(0.069)	(0.186)	(1.643)
HCH	−13.66	−9.22	−9.71	−0.19	0.191	5.236	0.621	0.703	0.662	
				(−0.164)	(0.215)	(4.651)	(0.536)	(0.714)	(0.625)	(2.493)
HCCH$_3$	−7.86			−0.153	0.173	5.78	0.5	0.539	0.52	
				(−0.133)	(0.186)	(5.376)	(0.492)	(0.493)	(0.492)	(2.645)
HCPh	−7.08			−0.15	0.127	7.874	0.29	0.255	0.273	
				(−0.127)	(0.137)	(7.299)	(0.316)	(0.285)	(0.301)	(2.306)
HCCl	2.24	6.4	6.39	−0.188	0.174	5.747	0.516	0.68	0.598	
				(−0.164)	(0.174)	(5.747)	(0.485)	(0.806)	(0.645)	(2.787)
ClCPh	4.59			−0.164	0.128	7.813	0.296	0.262	0.279	
				(−0.138)	(0.12)	(8.333)	(0.309)	(0.29)	(0.3)	(2.575)
ClCCH$_3$	4.94			−0.169	0.163	6.135	0.455	0.541	0.498	
				(−0.143)	(0.156)	(6.41)	(0.443)	(0.589)	(0.516)	(2.84)
HCF	12.13	14.7	15.83	−0.175	0.206	4.854	0.662	0.808	0.735	
				(−0.161)	(0.19)	(5.263)	(0.652)	(0.998)	(0.825)	(3.431)
FCPh	13.32			−0.158	0.145	6.897	0.445	0.227	0.336	
				(−0.136)	(0.122)	(8.197)	(0.36)	(0.324)	(0.342)	(2.951)
ClCCl	16.57	20.5	20.04	−0.203	0.168	5.952	0.491	0.667	0.579	
				(−0.173)	(0.144)	(6.944)	(0.46)	(0.883)	(0.671)	(3.194)
FCCl	33.42		37.09	−0.2	0.2	5.0	0.559	0.753	0.656	
				(−0.176)	(0.15)	(6.667)	(0.566)	(0.972)	(0.769)	(3.774)
ClCOCH$_3$	35.96			−0.156	0.194	5.155	0.511	0.693	0.602	
				(−0.148)	(0.143)	(6.993)	(0.512)	(0.784)	(0.648)	(3.58)
FCOCH$_3$	51.79			−0.145	0.227	4.405	0.735	0.747	0.741	
				(−0.142)	(0.152)	(6.579)	(0.648)	(0.837)	(0.742)	(4.263)
FCF	52.12	56.7	56.43	−0.192	0.246	4.065	0.819	0.902	0.861	
				(−0.178)	(0.164)	(6.098)	(0.757)	(1.075)	(0.916)	(4.616)
CH$_3$OCOCH$_3$	53.02			−0.108	0.215	4.651	0.654	0.762	0.708	
				(−0.118)	(0.146)	(6.849)	(0.592)	(0.641)	(0.616)	(4.055)
HOCOH	54.53			−0.117	0.233	4.292	0.745	0.857	0.801	
				(−0.13)	(0.167)	(5.988)	(0.7)	(0.753)	(0.727)	(4.192)

^{a} This study, 6-31G*/B3LYP values. ^{b} Experimental values, see ref 17. ^{c} GVB adjusted values from ref 17. ^{d} Chemical potential, au. ^{e} Hardness, au. ^{f} Softness, au^{-1}. ^{g} Carbene carbon condensed Fukui function for electrophilic attack.[19] ^{h} Carbene carbon condensed Fukui function for nucleophilic attack.[19] ^{i} Carbene carbon condensed Fukui function for radical attack.[19]
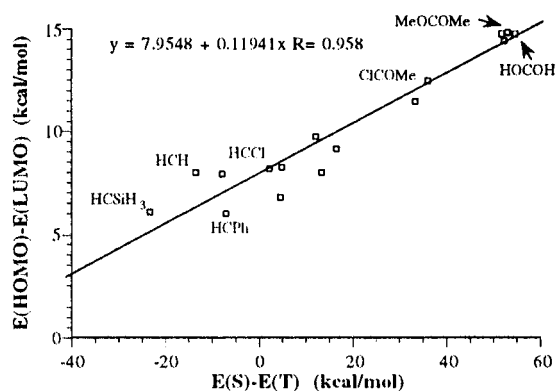

Figure 1. Correlation between the calculated HOMO−LUMO energy gap of the singlet carbenes and the singlet−triplet energy differences. A few points from Table 1 are identified in the graph.

equilibrium geometry of the neutral were used to determine several global and condensed HSAB-DFT parameters (Table 1). The chemical potential (μ), hardness(η), softness (S), as well as the carbene carbon condensed Fukui functions for electrophilic (s_C^-), nucleophilic (s_C^+), and radical attack (s_C^o) were calculated for the singlet and triplet states of each carbene. The chemical potential (μ), hardness(η), and softness (S) are global properties defined in terms of the ionization potential (I) and the electron affinity (A) by the expressions: $\mu = -(I + A)/2$, $\eta = (I - A)/2$, and $S = 1/\eta$, respectively.[2] Condensed properties are quantities that reflect how the electronic density at specific atom k in the molecule may respond to electronic perturbations resulting from removal or addition of charges. The condensed softness of atom k (s_k) is formulated in terms of a global softness (S) and a condensed Fukui function (f_k).[19] The Fukui function is a quantity related to the HOMO and LUMO orbital densities of the carbene after adding or subtracting one electron.[20] After analysis of a large data set obtained in this manner, from all the global and local quantities calculated, only the carbene carbon condensed softness for electrophilic attack of the triplet state, $s_C^-(T)$, showed a reasonably good correlation with the magnitude of the singlet−triplet gap over all the carbenes in the series ($r^2 = 0.932$, Figure 2). The $s_C^-(T)$ parameter comes from the softness of the triplet carbene weighed by the condensed Fukui function (f_C) at the carbene carbon ($s_C^- = Sf_C$).[2] The f_C reflects the change in electron density at the carbene carbon atom after an electron has been removed. Both f_C and s_C^- contain the same information about carbon atom reactivity in a carbene molecule, but s_C^- contains additional information about the carbene global softness. An increase in s_C^- has been qualitatively interpreted as the tendency of the carbon atom to give up its (negative) charge to incoming electrophiles.[1,9] That a good linear correlation can only be found with the triplet state suggests the importance of exchange interactions involved in determining the singlet−triplet gap which are absent in the singlet state. Large values of $s_C^-(T)$ for carbenes with large singlet−triplet gaps indicate that relatively high electronic densities would be left at the carbene carbon upon ionization

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Table 2.   Singlet State DFT Parameters in Atomic Units (au) for a Series of Alkenes Analyzed in this Study

alkene	$\mu_{calc}{}^a$ (μ_{exp})^b	$\eta_{calc}{}^c$ (η_{exp})^d	S^e	$f_{C_1}^-$ ($f_{C_2}^-$)^f	$f_{C_1}^+$ ($f_{C_2}^+$)^g	$f_{C_1}^0$ ($f_{C_2}^0$)^h
cyanoethylene	−0.175 (−0.198)	0.212 (0.206)	4.71	−0.030 (0.006)	0.366 (0.277)	0.168 (0.141)
ethylene	−0.129 (−0.162)	0.252 (0.228)	3.97	−0.108	0.498	0.195
trans-2-butene	−0.102 (−0.129)	0.226 (0.206)	4.42	−0.098	0.401	0.151
dimethyl-2-butene	−0.093 (−0.110)	0.206 (0.195)	4.85	−0.089	0.245	0.078

^{a} This study, chemical potential values, au. ^{b} Experimental values,[21] au. ^{c} This study, global hardness values, au. ^{d} Experimental values,[21] au. ^{e} Softness, au^{-1}. ^{f} Alkene carbon condensed Fukui function for electrophilic attack.[19] ^{g} Alkene carbon condensed Fukui function for nucleophilic attack.[19] ^{h} Alkene carbon condensed Fukui function for radical attack.[19]
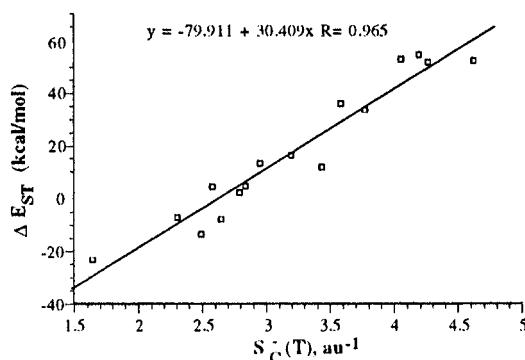
Figure 2. Correlation between the condensed softness for electrophilic attack of the carbene triplet-state carbon atom, s_C^-(T), and the singlet−triplet gap.

Scheme 2
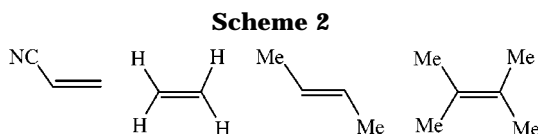
and reflect the extent of stabilization given by substituents. Interestingly, since the s_C^-(T) value contains information on how the entire electronic structure of the carbene affects the carbene carbon, the s_C^-(T) may account for the nonlinear contributions of inductive and resonance effects that escape the linear correlation of these two contributions to the Mulliken charges proposed by Goddard et al.[17]

DFT Analysis of Charge Transfer between Carbenes and Alkenes. The electronic structures of cyanoethylene, ethylene, *trans*-2-butene, and tetramethylethylene were analyzed at the same levels of theory as the structures of the carbenes (B3LYP/6-31G*, see Scheme 2 and Table 2). The structures and energies of the oxidized and reduced (cation and anion) species were calculated at the equilibrium geometry of the neutral for all the alkenes included in the study. An excellent correlation between calculated and experimentally derived hardness [$\eta = (I − A)/2$] and between calculated and experimentally derived electronic chemical potential [$\mu = −(I + A)/2$] confirmed the suitability of the functional.[21,22]

The interaction between alkenes and singlet carbenes was explored in a pair-wise manner. We reasoned that carbene electrophilicity and nucleophilicity can be analyzed in terms of trends in charge-transfer interactions that are latent within the structure of a given carbene against a set of increasingly electron-rich alkenes. Calculations at the global level are expected to reflect the initial charge transfer between the carbene and the

alkene as they begin forming the corresponding cyclopropane. The magnitude of this quantity reflects the perturbation of one molecule by another while they maintain their identities. Considerable charge-transfer tendencies (ΔN) from alkenes to carbenes were calculated in most cases by the electronegativity equalization principle (eq 1 and Figure 3).[3,22] Chemical potential differ-

$$\Delta N = \frac{1}{2} \frac{(\mu_{alkene} − \mu_{carbene})}{\eta_{alkene} + \eta_{carbene}} \quad (1)$$

ences (electronegativity differences) drive electron transfer (ΔN) and electrons tend to flow from a region of high chemical potential (low electronegativity) to a region of low chemical potential (high electronegativity).

For any given carbene, the extent of electron transfer from alkene to the carbene increased as the alkene became more electron-rich in the series: cyanoethylene < ethylene < *trans*-2-butene < tetramethylethylene. As expected, the extent of charge transfer varied substantially from carbene to carbene, and the net charge transfer calculated between cyanoethylene and ethylene with the most electron-rich carbenes was indeed from the carbene to the alkene. There is no correlation between singlet−triplet energy gaps and the extent of charge transfer towards a given alkene calculated by the electronegativity equalization principle. The charge transfer tendencies in Figure 3 order most ambiphilic and nucleophilic carbenes correctly according to Moss' carbene selectivity indices (given on top of each set in Figure 3).[10a] Although the location expected for ClCMe, ClCPh, and FCPh from product-determined carbene selectivity indices appears out of place, the results from charge transfer calculations with eq 1 are reminescent of the ambiphilicity documented with absolute rate measurements by Moss et al.[10c] Charge transfer from ClCMe, ClCPh, and FCPh to electron-poor cyanoethylene (Figure 3) suggests that phenyl and methyl substituents help accommodate a positive charge at the carbene carbon, rendering it electron donating.

Interaction Energies between Carbenes and Alkenes. Interaction energies between carbenes and alkenes, $(\Delta E_{int})_{AB}^{ab}$ can be calculated by eq 2 in a perturbational

$$(\Delta E_{int})\,_{AB}^{ab} \approx −\frac{1}{2} \frac{(\mu_A − \mu_B)^2}{S_a^q + S_b^q} (s_a^q\, s_b^q) − \frac{1}{2} \frac{\lambda}{S_a^q + S_b^q} \quad (2)$$

approximation that takes into account electron-density derived properties of the alkene (A) and the carbene (B) as well as specific carbon atoms (a and b) involved in the bond-making−bond-breaking processes.[24−28]

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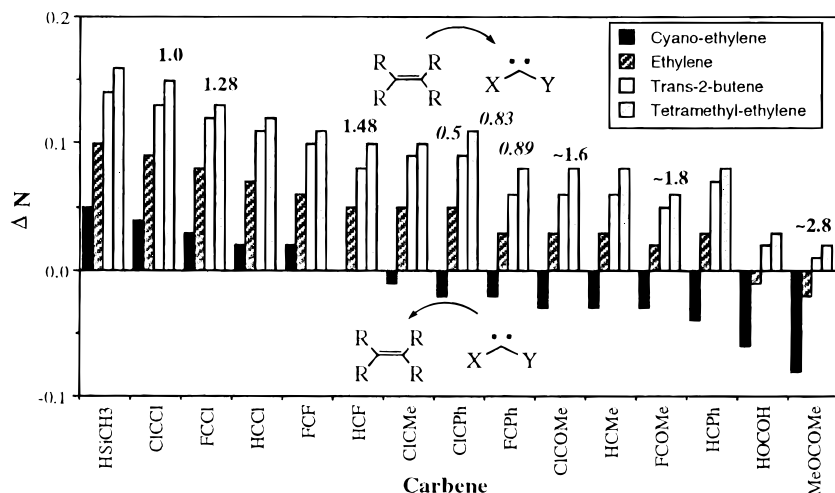
Figure 3. Histogram of charge transfer (ΔN) calculated by the electronegativity equalization principle between carbenes X–C–Y and tetramethylethylene, *trans*-2-butene, ethylene, and cyanoethylene. Negative values indicate transfer from the carbene to the alkene.

Among the DFT indices postulated to reflect the latent electrophilicity ($q = +$ in eq 2), nucleophilicity ($q = -$) and radicaloid ($q = $ o) interactions of atom $i =$ a, b (within molecules A and B) are the condensed softness for nucleophilic attack [s_i^+], the condensed softness for electrophilic attack [s_i^-], and the condensed softness for radical attack [s_i^o].[23] Notice that the superscript indicates the tendency of the atom to increase (+), reduce (−), or maintain (o) its charge. The interaction energies calculated with these quantities are reminiscent of those analyzed between different orbitals in an FMO perturbational analysis. In this case, there are nine interactions to be analyzed between a pair of bond-making–breaking atoms in each two reagents: i.e, carbene:alkene = +:+, +:−, +:o, etc. These interactions give an indication of electron flow between two prospective reagents and arise entirely from the electronic structure of the two components. It is assumed in this treatment that the more favorable interaction should reflect the tendency of the interacting species as they engage in a common electronic processes where the change is from reactants into products. The term λ in eq 2 depends on the number of valence electrons participating in the reaction. However, since λ has the same value for all interactions, a determination of its value is not necessary, and a value of one was utilized.[8]

Nine interactions energies $(\Delta E_{int})_{AB}^{ab}$ were calculated for each of the two spin states of all sixteen carbenes with each of the four ground-state alkenes. Qualitatively, it is expected that the relative magnitude of these interactions will reflect the most favorable pathway for electronic flow and electronic reorganization in going from reactants to products. Searching for general reactivity trends, one may look for interactions within each carbene–alkene pair, leading to the most negative values. As expected, triplet-state interaction energies were systematically smaller than those of the singlet-state carbene. In most cases, that the strongest interaction occurs

between the s_C^- of the singlet state carbene carbon and the s_C^- of the ground state alkene carbons. This remarkable result indicates that in most cases, both the carbene and the alkene have a tendency to reduce their negative charge (i.e., donate electrons) as they approach one another. The only exceptions were the phenyl-substituted carbenes which have a strongest interaction between the s_C^+ of the carbene carbon and the s_C^- of the alkene. This result is consistent with the tendency of the phenyl group to accommodate the additional negative charge received by the carbene carbon. The predominance of this interaction is a manifestation of the electrophilicity of the phenyl substituted carbenes, which is not as apparent in the charge-transfer analysis by the electronegativity equalization principle shown in Figure 3. Interestingly, although tendencies towards mutual electron donation occur in most cases, more charge is expected to be transferred from the alkene to the carbene than in the opposite direction. This was verified by analyzing the interaction energies between carbene carbons (local) and the entire alkene molecules (global) and between an alkene carbon (local) and the entire carbene molecule (global), which reveals overall charge transfer from alkene to carbene in each and every case.

Although the most important interaction energy can be identified for each pair of reactants, no comparisons are possible with different alkenes or carbenes. The two terms in the interaction energy equation (eq 2) have been interpreted in terms of charge-transfer interactions and electronic reorganization, respectively. The magnitude of the first term is usually small for neutral reactions and the addition of singlet carbenes to alkenes is no exception with as much as 99% of the interaction energy coming from the second term. The dominant nature of the s_C^- to s_C^- interaction reveals the relatively soft (polarizable) character of both alkenes and singlet carbenes. If viewed as an acid–base reaction, it would appear that the addition of carbenes to alkenes has indeed basic and acidic components from each of the two species as they are both ambiphilic. However, when net charge transfer is considered in a global to local manner, the basicity of the carbene appears to be rather weak as compared to

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its acidity, even when reacting with strongly electrophilic alkenes.

Conclusions

The electronic structures and electron density-derived interactions between a set of sixteen carbenes and four alkenes have been investigated. We confirmed that the singlet−triplet gaps calculated by DFT methods using the B3LYP functional correlate extremely well (within 2−4 kcal/mol) with experimentally known values for carbenes that span over 70 kcal/mol. A good correlation between the singlet−triplet gap and the condensed softness for electrophilic attack at the triplet carbene carbon atom [$s_C^-(T)$] reflects the stability of the carbene upon electron donation, along with electron-exchange interactions affecting the singlet−triplet gap. When the local interactions between carbenes and alkenes are considered, evidence for ambiphilic and nucleophilic character is observed as the direction of charge transfer calculated with the electronegativity equalization prin-

ciple changes in magnitude and sign with the carbene and alkene pair considered. However, analysis of global properties indicates that, in general, electron transfer always occurs from the alkene to the carbene carbon. It was also found that interaction energies between alkenes and carbenes are most favorable with local parameters that reflect mutual electron donation. The acidic and basic characteristics of carbenes and alkenes is therefore manifested in terms of a complex, mutual and unequal electronic flow.

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