On the Principle of Spin Potential Equalization

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In analogy with Sanderson's electronegativity equalization principle, it is possible to postulate a principle of spin potential equalization in the $E[N_\alpha, N_\beta]$ representation of the spin polarized density functional theory, where N_α and N_β refer to the number of electrons with spins α and β, respectively. The principle provides simple expressions to evaluate the energy changes ΔE between two interacting molecules, A and B, together with the electron transfer, ΔN_α and ΔN_β. The model is illustrated for a series of addition reactions of electrophilic, nucleophilic, and ambiphilic carbenes to alkenes in their singlet and triplet multiplicities. The results are in a consistent qualitative agreement with the experimental reactivity established for these systems.

1. Introduction

Almost all the applications of density functional theory to understand empirical chemical concepts such as electronegativity,[1-3] electrophilicity,[4] hardness,[5-7] and others are based on the first Hohenberg–Kohn theorem, which establishes that the energy and all other molecular properties are a functional of the density.[8] However, the functional is unknown, and one has to resort to approximated functionals, to bring more information to the functional, or both. It was very early realized that for systems bearing unpaired electrons, the separate consideration of the ρ_α and ρ_β spin components of the density is important to obtain meaningful information about the electronic structure of matter and its application to reactivity problems.[9-14] This consideration led to the formulation of the spin-polarized version of the density functional theory (SP-DFT), which has been in some aspects controversial because of the difficulties in the interpretation of the first Hohenberg–Kohn theorem: it is not trivial to find a one-to-one correspondence between ρ_α, ρ_β and some sort of spin potentials. The point has been recently addressed by Ayers and Yang.[15]

Having established the convenience of using a functional of $\rho_\alpha(r)$ and $\rho_\beta(r)$, it seems natural to make attempts to generalize some useful empirical chemical concepts, such as electronegativity, electrophilicity, hardness, and others, within the $\rho_\alpha(r)$ and $\rho_\beta(r)$ SP-DFT framework. Of course, for closed shell molecules, the generalized concepts converge to the standard ones;[16,17] however, they are essential for open-shell molecules for which the definition of the chemical potential in terms of the HOMO and LUMO orbital energies is still controversial. There are two representations for the spin-polarized version: one having ρ_α and ρ_β as the basic variables[18] and another in which the basic variables are ρ and ρ_s, where ρ_s is the spin density $\rho_s = \rho_\alpha - \rho_\beta$.[19,20] The issue of a spin polarized version of the chemical reactivity indices has been addressed in a series of works,[21,22]

and very recently, a comprehensive discussion has been published.[23] In this paper, we will elaborate further on the SP version of the concept of electronegativity in the search of a possible generalization of Sanderson's electronegativity equalization principle[24] defined within the spin-restricted DFT. The idea that some spin density redistribution process takes place prior to bond formation in diatomic molecules, therefore leading to the equalization of the spin potentials associated with the α and β spin densities, was implicitly introduced earlier by Ghanty and Ghosh.[18] These authors developed a simple chemical model of bonding in the $\rho_\alpha(r)$ and $\rho_\beta(r)$ representation in which the spin potential equalization was implicitly assumed to hold, but no formal basis to its justification was attempted. In this paper, a derivation of the generalized principle of spin potential equalization will be given, and the reliability of the model will be illustrated for a series of addition reactions of electrophilic, nucleophilic, and ambiphilic carbenes to alkenes in their singlet and triplet ground-state multiplicities.

2. Theoretical Aspects

Assuming that the external potential keeps constant and that the only change in the system is in the number of electrons with spin α or β, one can expand the total energy of a system with spin polarization as a function of N_α and N_β as

$$E[N_\alpha, N_\beta] = E[N_\alpha^0, N_\beta^0] + \mu_\alpha^0 \Delta N_\alpha + \mu_\beta^0 \Delta N_\beta + \frac{1}{2}\eta_{\alpha\alpha}^0 (\Delta N_\alpha)^2 + \frac{1}{2}\eta_{\beta\beta}^0 (\Delta N_\beta)^2 \quad (1)$$

where $E[N_\alpha^0, N_\beta^0]$ is the total energy of the reference system with N^0 electrons ($N^0 = N_\alpha^0 + N_\beta^0$). μ_α^0, μ_β^0, $\eta_{\alpha\alpha}^0$, and $\eta_{\beta\beta}^0$ are the corresponding first and second derivatives in the Taylor expansion. They are associated with the chemical potential and the hardness, respectively. Note that, as has been previously shown,[25,22] the crossed second derivative corresponding to $\eta_{\alpha,\beta}$ is exactly zero. The change in the number of electrons with spin σ is represented by ΔN_σ. From now on, we will assume that the derivative of the energy with respect to the number of electrons is well-defined (this assumption has recently been

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TABLE 1: Spin Chemical Potential ($\mu_\alpha^0 = \mu_\beta^0 = \mu_\sigma^0$) and Spin Chemical Hardness ($\eta_{\alpha\alpha}^0 = \eta_{\beta\beta}^0 = \eta_{\sigma\sigma}^0$) for Singlet Para-Substituted Phenylhalocarbenes (p-YPhXC) Series and Tetramethylethylene (TMET)

			X = F			
Y	μ_σ^0	$\eta_{\sigma\sigma}^0$	μ_σ^{FMO}	ΔN_σ	ΔE	μ_σ^{SPE}
NO$_2$	−5.03	2.76	−4.90	0.27	−0.68	−4.30
CN	−4.80	3.01	−4.38	0.24	−0.55	−4.09
CHO	−4.69	2.90	−4.43	0.23	−0.51	−4.03
F	−4.19	3.36	−3.50	0.17	−0.29	−3.62
H	−4.11	3.32	−3.49	0.16	−0.27	−3.58
CH$_3$	−3.96	3.36	−3.34	0.15	−0.22	−3.47
OH	−3.86	3.44	−3.09	0.14	−0.19	−3.39
OCH$_3$	−3.77	3.40	−3.01	0.13	−0.17	−3.34
NH$_2$	−3.51	3.41	−2.72	0.10	−0.11	−3.16
			X = Cl			
Y	μ_σ^0	$\eta_{\sigma\sigma}^0$	μ_σ^{FMO}	ΔN_σ	ΔE	μ_σ^{SPE}
NO$_2$	−5.11	2.42	−4.94	0.28	−0.75	−4.42
CN	−4.94	2.56	−4.37	0.26	−0.65	−4.27
CHO	−4.38	2.48	−4.43	0.25	−0.60	−4.21
F	−4.40	2.87	−3.55	0.20	−0.39	−3.83
H	−4.34	2.82	−3.57	0.19	−0.36	−3.79
CH$_3$	−4.20	2.84	−3.41	0.18	−0.31	−3.70
OH	−4.08	2.92	−3.14	0.16	−0.27	−3.60
OCH$_3$	−4.02	2.90	−3.09	0.16	−0.25	−3.56
NH$_2$	−3.73	2.96	−2.81	0.13	−0.16	−3.35
			X = Br			
Y	μ_σ^0	$\eta_{\sigma\sigma}^0$	μ_σ^{FMO}	ΔN_σ	ΔE	μ_σ^{SPE}
NO$_2$	−5.14	2.28	−4.84	0.29	−0.78	−4.48
CN	−4.96	2.46	−4.33	0.27	−0.66	−4.30
CHO	−4.83	2.39	−4.39	0.25	−0.60	−4.22
F	−4.42	2.77	−3.61	0.20	−0.40	−3.86
H	−4.35	2.73	−3.61	0.20	−0.37	−3.82
CH$_3$	−4.22	2.75	−3.47	0.18	−0.32	−3.72
OH	−4.09	2.86	−3.25	0.17	−0.27	−3.62
OCH$_3$	−4.02	2.84	−3.19	0.16	−0.25	− 3.57
NH$_2$	−3.76	2.88	−2.94	0.13	−0.17	−3.37
TMET	−2.46	6.94				

Spin chemical potential for the product of the cycloaddition reaction (μ_σ^{FMO} and μ_σ^{SPE}), estimated by frontier molecular orbital ($\mu_\alpha^{FMO} = \mu_\beta^{FMO} = \mu_\sigma^{FMO}$) and principle of spin potential equalization ($\mu_\alpha^{SPE} = \mu_\beta^{SPE} = \mu_\sigma^{SPE}$). Electron transfer ($\Delta N_\alpha = \Delta N_\beta = \Delta N_\sigma$) and energy changes ($\Delta E$) between interacting carbene−alkene molecules. Values calculated at B3LYP/6-31G(d) level. Values are in electron volts.

discussed[23]). Therefore, we will have only one value for all derivatives evaluated at integer numbers of electrons, independent of whether the derivation is done from the left or the right side. This is the standard model in the application of density functional theory to empirical concepts of chemistry. Now, following closely the model introduced in ref 26 for the case without spin polarization, consider systems A and B already at the equilibrium distance, and the electron cloud begins to reaccommodate to find the equilibrium at the minimum energy. The total energy is the sum of the energy changes in A and B due to the interchange of electrons of spin α or β, and using the Taylor series is given by

$$\Delta E = (\mu_{\alpha,A}^0 - \mu_{\alpha,B}^0)\Delta N_\alpha + (\mu_{\beta,A}^0 - \mu_{\beta,B}^0)\Delta N_\beta +$$
$$\frac{1}{2}(\eta_{\alpha\alpha,A}^0 + \eta_{\alpha\alpha,B}^0)(\Delta N_\alpha)^2 + \frac{1}{2}(\eta_{\beta\beta,A}^0 + \eta_{\beta\beta,B}^0)(\Delta N_\beta)^2 \quad (2)$$

The system will interchange electrons of spin α or β until the energy find a minimum. In doing so, the spin chemical potential of each species will also change. According to the Taylor series, this change is given by

$$\mu_{\sigma,M} = \mu_{\sigma,M}^0 + \eta_{\sigma\sigma,M}^0 \Delta N_{\sigma,M} \quad (3)$$

with $\sigma = \alpha$ or β and $M = A$ or B. Now, minimizing the total

energy with respect to the variations in the number of electrons with spin α and β one finds

$$\mu_{\alpha,A} = \mu_{\alpha,B} \quad (4)$$

and

$$\mu_{\beta,A} = \mu_{\beta,B} \quad (5)$$

It means the spin chemical potentials behave similar to the normal chemical potential and there exists a principle of spin chemical potential equalization. They can also be interpreted as a sort of spin electronegativity. The electrons with spin σ will flow from the region a higher μ_σ to the regions of lower μ_σ until the spin chemical potential of the whole system is constant everywhere. The change in the number of electrons will be given by

$$\Delta N_\alpha = \frac{(\mu_{\alpha,B}^0 - \mu_{\alpha,A}^0)}{(\eta_{\alpha\alpha,A}^0 + \eta_{\alpha\alpha,B}^0)} \quad (6)$$

and

$$\Delta N_\beta = \frac{(\mu_{\beta,B}^0 - \mu_{\beta,A}^0)}{(\eta_{\beta\beta,A}^0 + \eta_{\beta\beta,B}^0)} \quad (7)$$

and the energy gain is

$$\Delta E = -\frac{1}{2}\frac{\left(\mu_{\alpha,B}^0 - \mu_{\alpha,A}^0\right)^2}{\eta_{\alpha\alpha,A}^0 + \eta_{\alpha\alpha,B}^0} - \frac{1}{2}\frac{\left(\mu_{\beta,B}^0 - \mu_{\beta,A}^0\right)^2}{\eta_{\beta\beta,A}^0 + \eta_{\beta\beta,B}^0} \qquad (8)$$

This expression is in complete analogy with the one in the model without spin polarization. The interpretation is also identical. A great difference in spin chemical potential favors the electron interchange. Now, however, one can differentiate whether the system is interchanging electrons with spin α or β, which is in the ground of any spin multiplicity change. It is interesting to note that the present development it is not possible using N and N_s as basic variables without assuming from the beginning the conservation of the total spin angular momentum.

3. Results and Discussion

With the purpose of evaluating the principle of spin potential equalization, we have considered the carbene–alkene addition reactions, in which the carbenic center expands its valence electron number of six to eight. The carbenes are important reactive intermediates in organic synthesis, having two possible electronic states, singlet and triplet. Each state exhibits a different reactivity, and it is affected differently by substituents. Both singlet and triplet carbenes undergo addition reactions. According to Skell,[27] the stereochemistry about the original carbon–carbon double bond is maintained in the singlet carbene, whereas in the stepwise addition to the triplet state, the stereochemical information is lost. A feature of the carbene–alkene addition reaction is the response of the carbene to the alkene substituents. On the basis of experimental studies[28–33] and a frontier molecular orbital (FMO) model,[33–35] Moss classified the reactive nature of simple carbenes as electrophilic, nucleophilic, and ambiphilic.

Three carbene–alkene addition reactions series have been studied: the addition of para-substituted singlet phenylhalocarbenes (*p*-YPhXC) to tetramethylethylene (TMET), with X = F, Cl, and Br and Y = NO$_2$, CN, CHO, F, CH$_3$, OH, OCH$_3$, and NH$_2$ (1); and the addition of met- and para-substituted phenylcarbenes (YPhHC) in the triplet ground state to TMET (2). In the last reaction, the formed diradical is considered itself as the product of the reaction. The formation of the corresponding cyclopropane involves spin inversion, and the application of the principle of the spin potential equalization is at constant multiplicity. Finally, the carbenic philicity is analyzed in CCl$_2$, CH$_3$OCCl, and CH$_3$OCCH$_3$.

The electronic structure of the studied systems has been fully optimized at the B3LYP/6-31G(d) level of theory using the G03 suite of programs.[36] The spin chemical potentials and spin chemical hardness, μ_σ and $\eta_{\sigma\sigma}$ (for $\sigma = \alpha$ or β), respectively, have been calculated using the finite differences approximation in terms of the ionization energy (I_σ) and the electron affinity (A_σ) of an electron of spin σ,

$$\mu_\sigma = -\chi_\sigma = -\frac{1}{2}(I_\sigma + A_\sigma), \quad \eta_{\sigma\sigma} = (I_\sigma - A_\sigma) \qquad (9)$$

where I_σ and A_σ can be roughly approximated by the HOMO and LUMO energy, respectively.

$$\mu_\sigma = \frac{1}{2}(\varepsilon_\sigma^{HOMO} + \varepsilon_\sigma^{LUMO}), \quad \eta_{\sigma\sigma} = (\varepsilon_\sigma^{LUMO} - \varepsilon_\sigma^{HOMO}) \ (10)$$

The use of the orbital energies to calculate the chemical potentials, hardness, and other indices has been in previous works justified.[37,38]

3.1. Singlet Phenylhalocarbenes Addition to Tetramethylethylene. The spin chemical potential, μ_σ^0, and spin chemical hardness $\eta_{\sigma\sigma}^0$, (for $\sigma = \alpha$ and β), for the three series of singlet
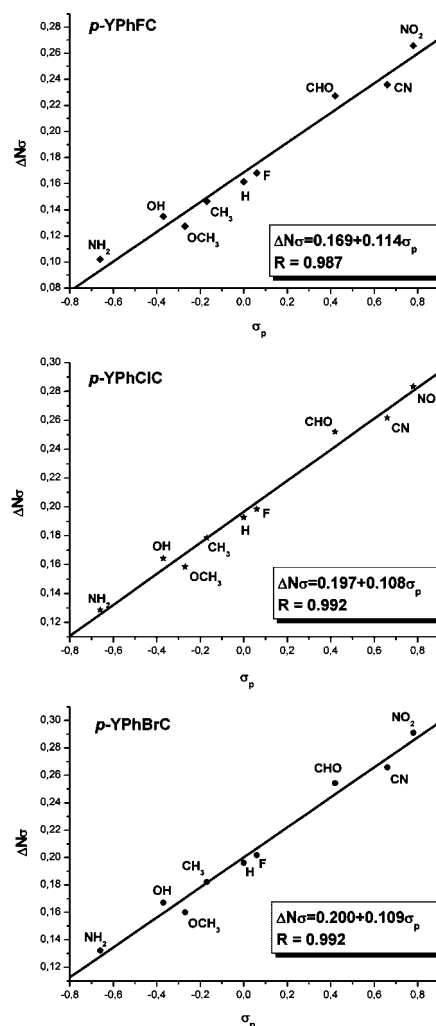
Figure 1. Plot of α and β spin electron transfer $\Delta N_\alpha = \Delta N_\beta = \Delta N_\sigma$ against Hammett parameters σ_p for addition reactions of the singlet para-substituted phenylhalocarbenes to tetramethylethylene

SCHEME 1
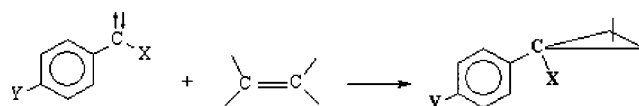
para-substituted phenylhalocarbenes (*p*-YPhFC, *p*-YPhClC, *p*-YPhBrC) are reported in Table 1. In this case, of course, the reactivity parameters for spins α and β are the same. In addition, in those tables are reported the spin chemical potentials of the product, μ_σ^{FMO} and μ_σ^{SPE}, calculated from frontier molecular orbital energies and from the equations of the principle of spin chemical potential equalization, eq 3, respectively. In the last two columns, we report the electron transfer, ΔN_σ (for $\sigma = \alpha$ and β), and the energy changes, ΔE, between the two interacting molecules. The difference in the spin chemical potentials leads to the flow of α and β electrons from regions of higher potential to regions of lower potential. For the three studied series, the electron transfer is from the TMET to the *p*-YPhXC. The spin chemical potential of TMET ($\mu_\sigma^0 = -2.46$ eV) is higher that the spin chemical potentials of the *p*-YPhXCs (column 2 in Table 1). Table 1 shows that ΔN_σ and ΔE for the addition of *p*-YPhXCs to TMET depend on the nature of the substituent. The μ_σ^0 and $\eta_{\sigma\sigma}^0$ values of the *p*-YPhXCs increase when the substituent in the aromatic ring increases its electron-donor effect. In

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TABLE 2: Spin Chemical Potential (μ_α^0 and μ_β^0) and Spin Chemical Hardness ($\eta_{\alpha\alpha}^0$ and $\eta_{\beta\beta}^0$) for Triplet Meta- and Para-Substituted Phenylcarbenes (YPhHC) Series and Tetramethylethylene (TMET), Calculated at the B3LYP/6-31G(d) Level[a]

Y		m-YPhHC				p-YPhHC		
	μ_α^0	μ_β^0	$\eta_{\alpha\alpha}^0$	$\eta_{\beta\beta}^0$	μ_α^0	μ_β^0	$\eta_{\alpha\alpha}^0$	$\eta_{\beta\beta}^0$
NO$_2$	−4.14	−5.17	3.24	5.02	−4.04	−5.46	3.84	4.34
CN	−3.61	−4.95	4.19	4.73	−3.28	−5.24	4.89	4.64
CHO	−3.65	−4.67	3.61	4.70	−3.44	−4.88	4.34	3.96
F	−2.72	−4.44	5.12	4.50	−2.72	−4.54	4.60	5.15
H	−2.54	−4.35	4.94	4.85	−2.54	−4.35	4.94	4.85
CH$_3$	−2.49	−4.16	4.91	4.62	−2.43	−4.26	4.80	4.91
OH	−2.44	−4.00	5.20	4.06	−2.38	−4.15	4.40	4.86
OCH$_3$	−2.35	−3.91	5.20	4.04	−2.30	−4.06	4.43	4.77
NH$_2$	−2.25	−3.60	5.19	3.66	−2.08	−3.75	4.25	4.48
TMET	−2.46		6.94					

[a] Values are in electron volts.

this sense, both reactivity parameters, μ_σ^0 and $\eta_{\sigma\sigma}^0$, contribute to the charge transfer from the TMET to the carbene. The charge transfer decreases with more electron-donor group. For example, in the p-YPhFC, ΔN_σ is 0.23 (Y = CHO) > 0.15 (Y = CH$_3$) > 0.13 (Y = OCH$_3$) > 0.10 (Y = NH$_2$). The electron-donor groups increase the electrostatic repulsion in the site of the reaction due to the inductive or conjugation effects (or both) exerted through the aromatic ring; therefore, the electronic transfer from the TMET to the carbenic carbon is less effective.

The substituent effects on the aromatic ring can be seen in terms of Hammett's substituent parameters (σ_p). σ_p values are derived from experiments in solvents of high polarity; therefore, they contain not only the intrinsic electronic contributions[39] but also the total electronic effects: field, inductive, resonance, and polarizability effects.[40−42] It is therefore interesting to compare the ΔN_σ values with the corresponding Hammet parameters. Figure 1 displays the correlation between the σ_p and the calculated ΔN_σ values for the addition reactions of the three singlet p-YPhXCs series to TMET. The σ_p values are taken from the compilations of Hammett parameters by Hansch, Leo, and Taft.[43] The ΔN_σ values are well-correlated with the σ_p constants, with correlation coefficients of 0.987, 0.992, and 0.992 for p-YPhFC, p-YPhClC, and p-YPhBrC, respectively. It is interesting to note that the ΔN_σ values, a quantity that reflects the perturbation of one molecule by other while maintaininig their identities, correlate well with a parameter that is completely experimental.

The results reported in Table 1 shows that the effect of the halogen atom bound to the carbenic carbon on the ΔN_σ and ΔE values decreases in the order Br > Cl > F when the substituent Y is the same group, although the electronegativity of the halogen atom suggests an opposite order. Inspection of $\eta_{\sigma\sigma}$ values for p-YPhXCs in the third column in Table 1 shows that η_σ^0 (p-YPhFC) > η_σ^0 (p-YPhClC) > η_σ^0 (p-YPhBrC) when the substituent is the same group. Accordingly, the electron transfer and energy changes due to halogen atoms are commanded by the spin chemical hardness rather than by its electronegativity, in agreement with the maximum hardness principle (MHP).[44,45]

The reactivity analysis described above is based on the principle of spin chemical potential equalization (SPE), according to eqs 4 and 5. To validate this hypothesis, the spin chemical potential of the product of the addition of p-YPhHC to TMET has been calculated by two methods: using the equations of SPE, eqs 3, 6, and 7, and using the frontier orbitals energy, eq 10. The obtained values (fourth and seventh columns in Table 1)

are very similar, which confirms that SPE is fulfilled for this series of addition reactions.

3.2. Triplet Phenylcarbenes Addition to Tetramethylethylene. Table 2 reports the spin chemical potentials, μ_α^0 and μ_β^0,

SCHEME 2
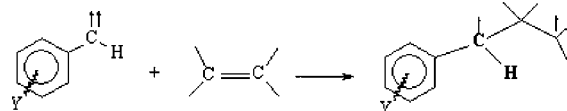
and the spin chemical hardness, $\eta_{\alpha\alpha}^0$ and $\eta_{\beta\beta}^0$, of the meta- and para-substituted phenylcarbenes (YPhHCs) and TMET on their triplet state. Table 3 shows spin chemical potentials for the intermediate diradical triplet, μ_α^{FMO}, μ_β^{FMO}, μ_α^{SPE}, and μ_β^{SPE}, calculated from the frontier molecular orbital energy and principle of spin chemical potential equalization, respectively. Additionally, α and β electron transfer ΔN_α and ΔN_β from TMET to YPhHC. The corresponding energy changes, ΔE_α and ΔE_β, are reported in Table 3. In this reaction, only the YPhHCs substituted using strong electron-withdrawing groups (NO$_2$, CN, and CHO) displays a significant α-electron transfer. For the other groups, the electron transfer is almost negligible. YPhHCs in its triplet ground state accepts β electrons of the TMET to form a new bond; therefore, the β electron transfer is significantly greater than the one of α electrons, as can be observed in Table 3.

The electron-donor groups (such as CH$_3$, OCH$_3$, OH, and NH$_2$) at the meta or para position decrease the ΔN_β values slightly from that of the parent YPhC (see Table 3). On the other hand, the electron-withdrawing groups at the meta or para position increase the ΔN_β values due to the increase in the electrophilic character of the carbenic carbon. Electron-withdrawing groups at the para position increase the ΔN_β value more than at the meta position. Accordingly, in these addition reactions, only the groups classified as strong electron-withdrawing display appreciable mesomeric effects. The difference in ΔN_β values between the meta and para-substituted molecules can be seen in Table 3. Figure 2 displays the correlation between the ΔN_β and Hammett substituent constants, σ_m and σ_p, for the addition of the triplet YPhHCs to TMET series. A better correlation was found for p-YPhHCs with a correlation coefficient of $R = 0.986$, whereas for m-YPhHCs, $R = 0.930$.

Energy changes were calculated for each of the two spin states of the PhHC addition to TMET. Qualitatively, the relative

TABLE 3: Electron Transfer (ΔN_α and ΔN_β) and Energy Changes (ΔE_α and ΔE_β) between Carbene–Alkene Interacting for Addition Reactions of the Triplet Meta- and Para-Substituted Phenylhalocarbenes to Tetramethylethylene[a]

				m-YPhHC				
Y	ΔN_α	ΔN_β	ΔE_α	ΔE_β	μ_α^{FMO}	μ_β^{FMO}	μ_α^{SPE}	μ_β^{SPE}
NO$_2$	0.17	0.23	−0.14	−0.31	−3.63	−4.98	−3.61	−4.03
CN	0.10	0.21	−0.06	−0.27	−3.08	−4.77	−3.17	−3.94
CHO	0.11	0.19	−0.07	−0.21	−3.21	−4.58	−3.24	−3.78
F	0.02	0.17	0.00	−0.17	−2.31	−4.29	−2.61	−3.66
H	0.01	0.16	0.00	−0.15	−2.19	−4.22	−2.51	−3.57
CH$_3$	0.00	0.15	0.00	−0.13	−2.11	−4.07	−2.48	−3.48
OH	0.00	0.14	0.00	−0.11	−2.11	−3.85	−2.45	−3.43
OCH$_3$	−0.01	0.13	0.00	−0.10	−2.09	−3.77	−2.40	−3.38
NH$_2$	−0.02	0.11	0.00	−0.06	−1.97	−3.52	−2.34	−3.20

				p-YPhHC				
Y	ΔN_α	ΔN_β	ΔE_α	ΔE_β	μ_α^{FMO}	μ_β^{FMO}	μ_α^{SPE}	μ_β^{SPE}
NO$_2$	0.15	0.27	−0.12	−0.40	−3.47	−5.23	−3.47	−4.30
CN	0.07	0.24	−0.03	−0.33	−2.80	−5.02	−2.94	−4.12
CHO	0.09	0.22	−0.04	−0.27	−2.98	−4.71	−3.06	−4.00
F	0.02	0.17	0.00	−0.18	−2.38	−4.40	−2.61	−3.65
H	0.01	0.16	0.00	−0.15	−2.19	−4.22	−2.51	−3.57
CH$_3$	0.00	0.15	0.00	−0.14	−2.12	−4.16	−2.44	−3.51
OH	−0.01	0.14	0.00	−0.12	−2.11	−3.98	−2.41	−3.45
OCH$_3$	−0.01	0.14	0.00	−0.11	−2.05	−3.91	−2.36	−3.40
NH$_2$	−0.03	0.11	−0.01	−0.07	−1.86	−3.62	−2.23	−3.24

[a] Estimated by frontier molecular orbital (μ_α^{FMO} and μ_β^{FMO}) and principle of spin potential equalization (μ_α^{SPE} and μ_β^{SPE}). Spin chemical potential for the intermediate diradical (μ_α^{FMO}, μ_β^{FMO} and μ_α^{SPE}, μ_β^{SPE}). Values calculated at B3LYP/6-31G(d) level. Values are in electron volts.
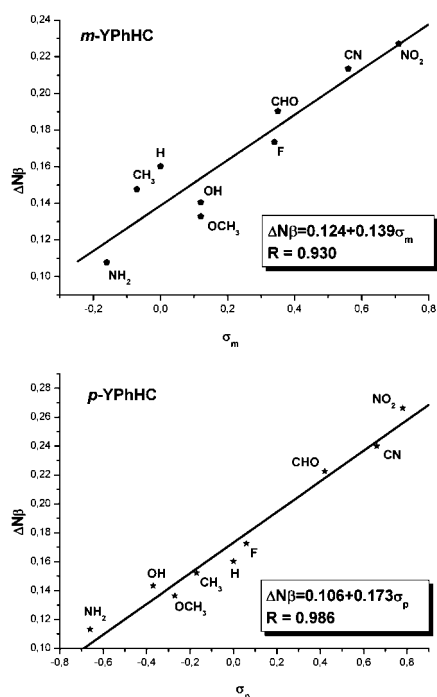
Figure 2. Plot of β spin electron transfer, ΔN_β, against Hammett parameters σ_m and σ_p for addition reactions of the triplet meta- and para- substituted phenylhalocarbenes to tetramethylethylene, respectively.

TABLE 4: Spin Chemical Potential ($\mu_\alpha^0 = \mu_\beta^0 = \mu_\sigma^0$) and Spin Chemical Hardness ($\eta_{\alpha\alpha}^0 = \eta_{\beta\beta}^0 = \eta_{\sigma\sigma}^0$) for the Carbenes and Alkenes Studied[a]

Alkene	μ_σ^0	$\eta_{\sigma\sigma}^0$
(CH$_3$)$_2$C=C(CH$_3$)$_2$	−2.46	6.94
	−2.25	12.72
(CH$_3$)$_2$C=CHCH$_3$	−2.69	6.90
	−2.38	13.10
(CH$_3$)$_2$C=CH$_2$	−2.83	7.37
	−2.60	13.50
trans-CH$_3$CH=CHCH$_3$	−2.70	7.38
	−2.36	13.78
CH$_2$=CHCOOCH$_3$	−4.31	6.17
	−4.03	13.35
CH$_2$=CHCN	−4.70	6.34
	−4.24	12.96

Carbene	μ_σ^0	$\eta_{\sigma\sigma}^0$
Cl$_2$C	−5.46	3.81
	−5.08	11.80
ClCH$_3$OC	−4.10	5.15
	−3.83	13.48
CH$_3$CH$_3$OC	−2.87	4.75
	−2.67	13.37

[a] All quantities are in electron volts. First entry corresponds to B3LYP/6-31G(d); second entry corresponds to MP2/6-311G(d,p).

magnitude of these interactions reflects the most favorable pathway for flow of the β electrons in going from reactants to a diradical intermediate. It is expected that the energy changes of the YPhHCs substituted with an electron-withdrawing group (NO$_2$, CN, CHO) are systematically greater than the YPhHCs substituted with an electron-donor group (CH$_3$, OH, OCH$_3$, and NH$_2$).

The similarity between μ_σ^{FMO} and μ_σ^{SPE} values (for $\sigma = \alpha$ and β) confirms again that the principle of spin chemical potential equalization is fulfilled for the addition reactions of the triplet meta- and para-substituted YPhHCs to TMET

3.3. Addition of Electrophilic, Nucleophilic and Ambiphilic Carbenes to a Set of Sustituted Alkenes. The philicity of the carbenes allows evaluation of the principle of spin chemical potential equalization in a set of addition reactions in which the net flow of electrons does not occur from the alkene to carbene. For example, ambiphilic carbene reacts as electrophiles with electron-rich alkenes but as nucleophiles with electron-poor alkenes. To evaluate the electron transfer (ΔN_σ for $\sigma = \alpha$ and β) between electrophilic (CCl$_2$), ambiphilic (CH$_3$OCCl), and nucleophilic (CH$_3$OCCH$_3$) carbenes and a set

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TABLE 5: Electron Transfer ($\Delta N_\alpha = \Delta N_\beta = \Delta N_\sigma$) between Carbene−Alkene Interacting[a]

alkene	Cl$_2$C			ClCH$_3$OC			CH$_3$CH$_3$OC		
	ΔN_σ	μ_σ^{SPE}	μ_σ^{FMO}	ΔN_σ	μ_σ^{SPE}	μ_σ^{FMO}	ΔN_σ	μ_σ^{SPE}	μ_σ^{FMO}
(CH$_3$)$_2$C=C(CH$_3$)$_2$	−0.28	−4.39	−3.57	−0.14	−3.40	−3.03	−0.04	−2.70	−2.08
	−0.12	−3.72	−3.35	−0.06	−3.02	−3.17	−0.02	−2.46	−2.90
(CH$_3$)$_2$C=CHCH$_3$	−0.26	−4.47	−3.61	−0.12	−3.49	−3.05	−0.02	−2.79	−2.05
	−0.11	−3.80	−3.37	−0.05	−3.09	−3.17	−0.01	−2.52	−2.93
(CH$_3$)$_2$C=CH$_2$	−0.24	−4.56	−3.71	−0.10	−3.58	−3.14	0.00	−2.85	−2.06
	−0.10	−3.92	−3.34	−0.05	−3.22	−3.20	0.00	−2.64	−2.96
trans-CH$_3$CH=CHCH$_3$	−0.25	−4.52	−3.67	−0.11	−3.52	−3.12	−0.01	−2.80	−1.98
	−0.11	−3.82	−3.28	−0.05	−3.10	−3.14	−0.01	−2.52	−2.92
CH$_2$=CHCOOCH$_3$	−0.11	−5.02	−4.11	0.02	−4.20	−3.64	0.13	−3.50	−3.32
	−0.04	−4.58	−3.85	0.01	−3.93	−3.50	0.05	−3.35	−3.39
CH$_2$=CHCN	−0.07	−5.17	−4.53	0.05	−4.37	−4.07	0.17	−3.65	−3.19
	−0.03	−4.68	−4.15	0.02	−4.04	−3.81	0.06	−3.47	−3.47

[a] Spin chemical potential for the product of the cycloaddition reaction (μ_σ^{FMO} and μ_σ^{SPE}). Estimated by frontier molecular orbital ($\mu_\alpha^{FMO} = \mu_\beta^{FMO} = \mu_\sigma^{FMO}$) and principle of spin potential equalization ($\mu_\alpha^{SPE} = \mu_\beta^{SPE} = \mu_\sigma^{SPE}$). Values are in *eV*. First entry corresponds to B3LYP/6-31G(d); second entry corresponds to MP2/6-311G(d,p).

of substituted alkenes, the spin chemical potential and spin chemical hardness (see Table 4) of all carbenes and alkenes have been calculated. Table 5 shows the results obtained for the electron transfer as well as the spin chemical potentials calculated for each of the cycloaddition products using both the FMO and SPE methods. In this case, the parameters have been calculated at two levels of theory, B3LYP/6-31G(d) and MP2/6-311G(d,p). In the latter case, the orbital energies are, of course, the Hartree−Fock ones. However, the MP2 geometry optimization has a significant influence on the electronic properties. In Table 5, it can be observed that the MP2 μ_σ^{SPE} and μ_σ^{FMO} values are closer to each other than the B3LYP values. The optimization of the molecular geometry at MP2 improves the results considerably. The difference between the ΔN_σ values at both theory levels is a consequence of the difference between the $\eta_{\sigma\sigma}^0$ values (Table 4). Hartree−Fock LUMO energies are always positive, which is not true for the LUMO energy obtained with B3LYP. Nevertheless, the tendency in the values of ΔN_σ is the same within each group. Negative values of ΔN_σ indicate transfer from the alkene to the carbene. ΔN_σ values show that CCl$_2$ exhibits electrophilic selectivity over the alkene set of Table 5. One can also see that the electron transfer is greater with highly alkylated alkenes, (CH$_3$)$_2$C=C(CH$_3$)$_2$, (CH$_3$)$_2$C=CHCH$_3$, (CH$_3$)$_2$C=CH$_2$, *trans*-CH$_3$CH=CHCH$_3$, and smaller with electron-poor alkenes such as CH$_2$=CHCOOCH$_3$ and CH$_2$=CHCN. In contrast, the ΔN_σ values for CH$_3$CH$_3$OC show that there is no appreciable electron transfer with electron-rich alkenes, whereas with electron-poor alkenes, the ΔN_σ values are high, and the electron transfer is from carbene to alkene(ΔN_σ = 0.13 for CH$_2$=CHCOOCH$_3$ and ΔN_σ = 0.17 for CH$_2$=CHCN), revealing the nucleophilic character of this carbene. The ambiphilic character of the ClCH$_3$OC is demostrated correctly. For the electron-rich alkenes, the electron transfer is from the alkene to the carbene, whereas with electron-poor alkenes, it is in the opposite direction.

In summary, a principle of spin chemical potential equalization has been established. Using N_α and N_β as independent variables allows us to complete the spin polarized version of the chemical reactivity model within density functional theory in close analogy to its original nonpolarized version. The equations have been successfully applied to a variety of addition reactions in singlet and triplet multiplicities. Note that for closed shell molecules, the results remain the same; however, for open shell molecules, the generalized definitions provide a more suitable and nonambiguous framework to discuss the reactivity of these systems.

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