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A Configuration Mixing Approach to the Reactivity of Carbene and Carbene Analogs

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Chemical addition is probably one of the most important reactions in catalytic processes. For example, the oxidative addition of transition metals[1] and insertion reactions involving organic fragments such as carbene[2] are crucial from both commercial and scientific standpoints. It is therefore not surprising that much experimental and theoretical work has been devoted to the study of the nature and energy sequence of such addition reactions, since a knowledge of the factors determining them is fundamental to the understanding of many reactions. However most of this work has been directed toward the problem of synthesis, reaction pathways, transition states and activation energies, etc. In this work, we will present a simple qualitative model in order to help us understand the origin of barrier heights and to obtain information about the electronic factors controlling them. The concept of barrier heights in such addition reactions may be understood by using the configuration mixing (CM) model, which is based on the theory by Pross and Shaik.[3] For simplicity, we take the insertion reaction XYC: + CH_4 as an example (see Figure 1).

In addition reactions the σ-bond may exist in a number of predetermined states, each of which may be approximated by the appropriate molecular orbital configuration. Possible states are ϕ_0, the ground singlet state $^1CXY-^1CH_4$; ϕ_1, the first excited triplet state $^3CXY-^1CH_4$; ϕ_2, the second excited triplet state $^1CXY-^3CH_4^*$; and ϕ_3, the excited ditriplet state $^3CXY-^3CH_4^*$. Consequently the reaction complex at any point on the reaction profile can be described by Ψ, which has the form

$$\Psi = a\phi_0 + b\phi_1 + c\phi_2 + d\phi_3 \qquad (1)$$

As in the two-configuration case,[4] ϕ_0 describes the reactant molecule in the ground state but an excited configuration in the product region, whereas ϕ_3 represents an excited reactant configuration but is the predominant descriptor of the products in their ground state. Note that the product configuration, ϕ_3, which arises from the excitation of XYC: and $CH'H_3$ to the ditriplet (overall singlet) state, allows both C−H and C−C bond formation and simultaneous C−H′ bond breaking. On the other hand, the intermediate configurations, ϕ_1 and ϕ_2, have triplet reactant−product spin-coupling (illustrated by the light curves) and would represent excited states at both the beginning and the end of the reaction. Therefore it is clear that at both reaction terminals the coefficients of ϕ_1 and ϕ_2 will be small and the reaction will be dominated by either ϕ_0 or ϕ_3. However, in the transition state region, ϕ_1 and ϕ_2 may be of similar energy to ϕ_0 and ϕ_3 and might therefore play an important role in describing the reaction complex, but since we are only concerned with singlet states and both ϕ_1 and ϕ_2 are triplet states, it can be assumed that ϕ_1 and ϕ_2 contribute very little, if at all, to Ψ. Instead, ϕ_0 and ϕ_3 are the main components of the reaction profile Ψ, and ϕ_1 and ϕ_2 may be neglected. Consequently, the reaction mechanism, in a qualitative manner, will be governed by the nature of the configurations from which the profile is built up, and the character of the transition state will reflect the extent to which the configurations mix into its wave function. Furthermore, since the barrier height is basically governed by the avoided crossing of the configurations ϕ_0 and ϕ_3 , it is easy to see that a $\phi_0 \rightarrow \phi_3$ excitation will correlate with the barrier, i.e. both ΔE_{st} ($\Delta E_{st} = E_{triplet} - E_{singlet}$ for carbene) and $\Delta E_{\sigma\sigma^*}$ ($\Delta E_{\sigma\sigma^*} = E_{triplet} - E_{singlet}$ for CH_4). It has to be pointed out that, basically, ϕ_3 is energetically dominated by $\Delta E_{\sigma\sigma^*}$ rather than by ΔE_{st} . If a substituent is introduced into the system which has the effect of stabilizing ϕ_3, then ϕ_3 will be displaced to a lower energy along the entire reaction coordinate (see Figure 2). The effect of such a perturbation is predicted (i) to reduce the reaction barrier since the intended crossing of ϕ_0 and ϕ_3 is lower in energy, (ii) to produce a larger exothermicity since the energy of the product is now lower than that of reactant, and (iii) to lead to an earlier transition state since the intended crossing point is now earlier along the reaction coordinate. Since (i) and (ii) provide energetic information and (iii) provides structural information, albeit at a qualitative level, the CM model presented here appears to explain the results of many similar singlet addition reactions. It should be noted that the predictions from the CM model are basically in accordance with Hammond's rule.[5]

From the above analysis, it is easy to predict that if $\Delta E_{\sigma\sigma^*}$ is a constant, then a small value of ΔE_{st} corresponds to a low barrier height and a large exothermicity. In other words, the relative stabilities of the lowest singlet and triplet states are in turn a sensitive function of the barrier height for carbenic reactivity. Despite the fact that the estimated magnitude of the barrier and the predicted geometry of the transition state for the insertion reaction appear to be dependent on the calculational level applied,[6] our qualitative predictions are in reasonable agreement with the reported results. For example, it is well established that insertion of H_2C: in its $^1A_1$ state into H_2 occurs without any barrier[7] but a barrier definitely exists for the

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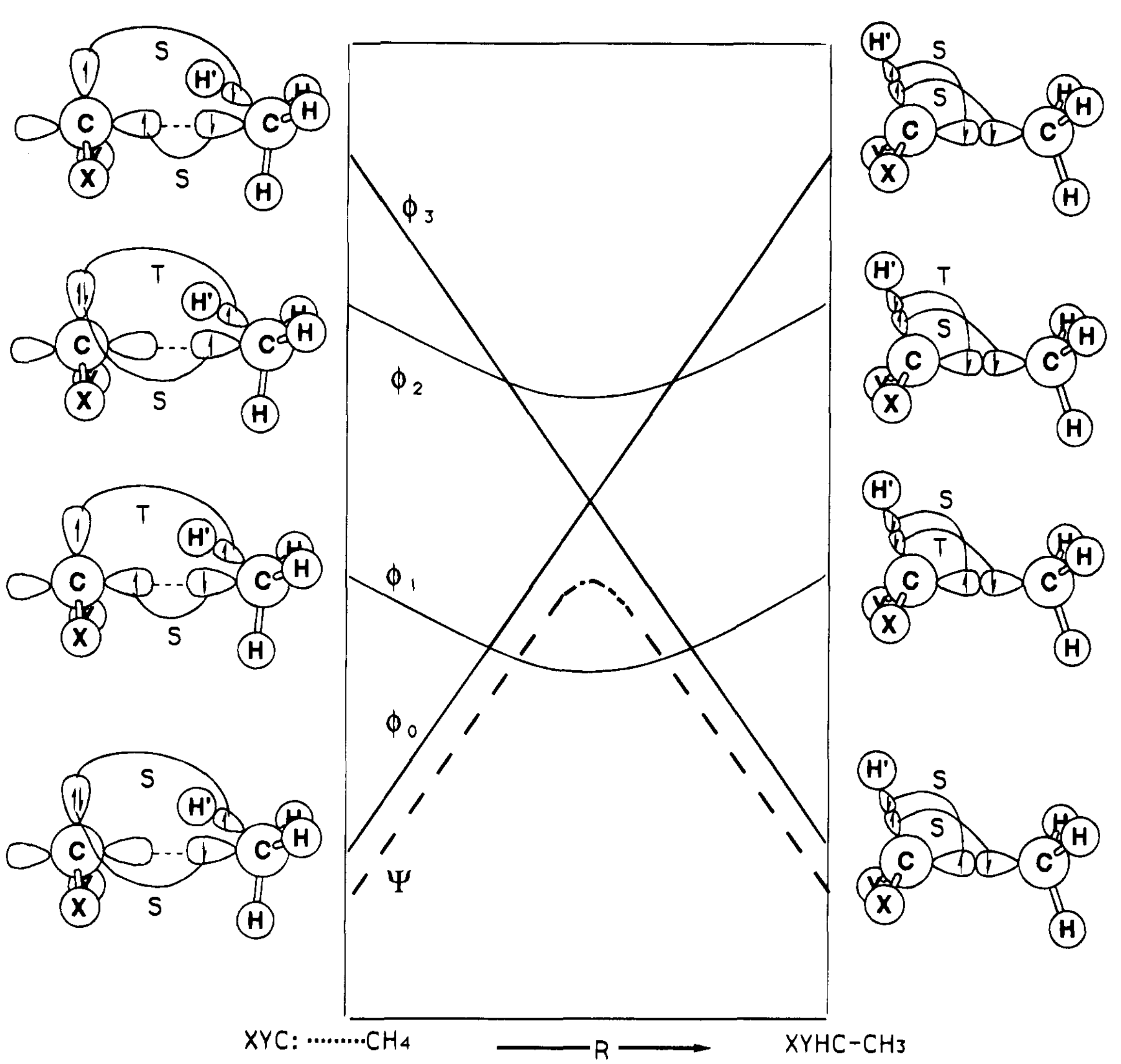

Figure 1. Energy diagram for a chemical addition showing the formation of a state curve (Ψ) by mixing four configurations: ϕ_0, the reactant configuration, ϕ_3, the product configuration, and ϕ_1 and ϕ_2, the intermediate configurations. S stands for singlet and T for triplet.

corresponding silylene reaction,[8] the reason for this being that the ground state is a triplet state in the former while it is a singlet state in the latter as we showed earlier. In addition to this, the order of activation energies for the insertion of a carbene species into CH_4 is H_2C: (2.8 kcal/mol) < HFC: (14.8 kcal/mol) < $H_2C{=}C$: (20.0 kcal/mol) < F_2C: (43.3 kcal/mol) since the corresponding values of ΔE_{st} are −22.1, 7.69, 38.5, and 51.3 kcal/mol, respectively,[9] while the insertion of a silylene species into SiH_4 involves activation energies of H_2Si: (0.3 kcal/mol) < $(CH_3)_2Si$: (10.4 kcal/mol) < HFSi: (13 kcal/mol) < Cl_2Si: (25 kcal/mol) < F_2Si: (39 kcal/mol) in accordance with their values of ΔE_{st} which are 12.9, 20.5, 34.6, 48.7, and 71.0 kcal/mol, respectively.[10] Such a barrier trend can also be found in the insertion of carbene into C_2H_6[9] and the corresponding reaction with silylene.[10] Moreover, since carbene insertion is an exothermic reaction, as shown previously, the barrier will decrease as the reaction exothermicity increases and the structure of the transition state will be similar to one of the reactants. From a systematic study of the possible influence of substituents on the insertion of silylene into H_2, which included the series H_2Si:, HFSi:, and F_2Si:, it was found that as the number of fluorine substituents increased the transition structure occurred progressively later along the reaction path while the exothermicity decreased.[11] A similar trend can also be found in the same reaction with the corresponding methylene series.[12] Our predictions can also be applied to systems in which carbene adds across a π bond. For instance, it was shown that the activation energies for addition to ethylene are in the order H_2C: (−24 to −52 kcal/mol) < Cl_2C: (8 kcal/mol) < F_2C: (25 kcal/mol) < F(OH)C: (34 kcal/mol) < $(OH)_2C$: (44 kcal/mol) since the corresponding values for ΔE_{st} are −22, 13, 51, 59, and 65 kcal/mol, respectively.[13] The analogous barrier trend for the carbene addition reaction also exists in the acetylene

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(11) (a) See ref 8. (b) The order of activation energies for insertion into H_2 is H_2Si: (9.1 kcal/mol) < HFSi: (29 kcal/mol) < F_2Si: (63 kcal/mol); their ΔE_{st} values are 13, 39, and 72 Kcal/mol, respectively.[10e]

(12) (a) See ref 8. (b) The order of activation energies for insertion into H_2 is H_2C: (−2.4 kcal/mol) < HFC: (11 kcal/mol) < F_2C: (44 kcal/mol); their ΔE_{st} values are −22, 7.7, and 51 kcal/mol, respectively.[10e]

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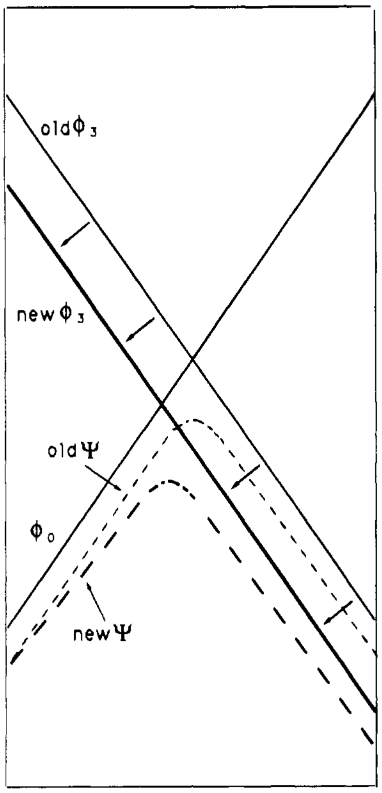

Figure 2. Energy diagram for a chemical addition described by two configurations that shows the effects of stabilizing the product configuration ϕ_3 (indicated by the arrows).

system.[14] It should be mentioned that our prediction for the carbene species addition into ethylene is similar to that found in the work of Pross and Moss.[3e]

On the other hand, if the value of ΔE_{st} is invariable, then a small value of $\Delta E_{\sigma\sigma^*}$ leads to a low barrier height. For example, the activation energy for the singlet silylene insertion reaction[15] increases in the order $H-SiH_3$ (0.3 kcal/mol; $\Delta E_{\sigma\sigma^*} = 192$ kcal/mol) < $F-SiH_3$ (8.3 kcal/mol; $\Delta E_{\sigma\sigma^*} = 198$ kcal/mol). The same reaction leads to a decreasing trend in activation energy for $H-NH_2$ (38 kcal/mol; $\Delta E_{\sigma\sigma^*} = 181$ kcal/mol) > $H-PH_2$ (20 kcal/mol; $\Delta E_{\sigma\sigma^*} = 143$ kcal/mol),[16] and similarly for $H-OH$ (22 kcal/mol; $\Delta E_{\sigma\sigma^*} = 186$ kcal/mol) > $H-SH$ (13 kcal/mol; $\Delta E_{\sigma\sigma^*} = 140$ kcal/mol)[17] and $H-F$ (10 kcal/mol; $\Delta E_{\sigma\sigma^*} = 242$ kcal/mol) > $H-Cl$ (8 kcal/mol; $\Delta E_{\sigma\sigma^*} = 177$ kcal/mol)).[16] It is worth noting that according to our predictions the order of exothermicity for the singlet insertion reactions mentioned above correlates directly with the barrier heights, which have already been verified in related references. Many other interesting examples can be found in refs.[18-20]

Therefore a knowledge of the ground spin state and the singlet–triplet splitting (ΔE_{st}) is of great importance in understanding such chemical addition reactions. Whether the ground state of XYC: is a triplet or singlet is determined by the substituents X and Y.[21] In general, the singlet state is stabilized by electron-withdrawing substituents and by substituents donating pπ lone pairs to the empty carbon pπ orbital whereas the triplet state is favored by substituents which are more electropositive than carbon and by sterically bulky substituents.

Furthermore, the isolobe analogy,[22] which provides a structural isomorphism between organic and organometallic fragments, has proven to be helpful in understanding the bonding in some peculiar transition metal complexes. It can be seen that our earlier predictions from the CM model might occur in the oxidative-addition reactions of transition metal systems. Methylene, H_2C:, is isolobal to d^{10} ML_2, d^9 MCpL, d^8 ML_4, d^8 ML_3, d^7 $MCpL_2$, d^6 ML_5, d^4 MCp_2L, and d^0 MCp_2L_2, and therefore it can be predicted that those compounds which have a ground triplet state will give singlet addition reactions which have a low barrier and a large exothermicity. Ziegler et al. have reported that the activation energies for the addition of H_2 to $RhCp(PH_3)$, $IrCp(PH_3)$, RhCp(CO), and IrCp(CO) fragments are nearly zero since they have negative values for ΔE_{st},[23] but those of $Ru(CO)_4$ and $Os(CO)_4$ fragments are 0.72 and 2.6 kcal/mol since their values of ΔE_{st} are 8.8 and 10 kcal/mol, respectively.[23] Likewise, the barriers for the addition of CH_4 to $Ru(CO)_4$ and $Os(CO)_4$ fragments are 18.9 and 24.1 kcal/mol, respectively.[23] Furthermore, it was found that the insertion of a $Pt(PH_3)_2$ fragment across an $H-SiH_3$ bond is easier than insertion across an $H-CH_3$ bond[24] due to a lower activation barrier and a larger exothermicity. This is because the value of $\Delta E_{\sigma\sigma^*}$ for SiH_4 (192 kcal/mol) is smaller than that for CH_4 (273 kcal/mol)[10e] as mentioned previously. Many other interesting examples can be found in refs[25-29]. Certainly, the analysis of such fine properties as the barrier height and the exothermicity requires special computational studies in addition to a careful review of the existing experimental data. Such studies, however, are beyond the scope of the present work.

Moreover, theoretically, since H_2C: is also isolobal to BH_3, AlH_3, CH_3^+, SiH_3^+, NH, PH, OH^+, O, and S, as well as to the Ni, Pd, and Pt family,[22] we may then foresee that an analogous

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effect can also be found in those systems (see refs 30−34). For instance, it is well-known that singlet species such as ^{1}O and ^{1}S react much more readily in singlet addition reactions without barriers than do ^{3}O and ^{3}S.[30] Likewise, since the ground state of the Pd atom is a d^{10} (singlet) state while that of the Pt atom is an s^1d^9 (triplet) state, the latter is a good model for facile oxidative addition processes.[31] From the above discussions, the relatively good agreement between the reported results and our predictions gives us confidence in using the CM model. Hence, it may be extended to other similar singlet carbenic reactions, such as organometallic systems which can undergo intramolecular insertions, rearrangements, intramolecular migrations, exchange reactions, reductive eliminations, and other reactions. Further studies will be discussed elsewhere.

Finally, one may wonder why the perturbation molecular orbital (PMO) analysis[35] does not provide a good explanation for carbenic reactivities. The present study shows that the favorability of such chemical reactions cannot be found using the MO model alone since other correlated configurations must be considered in the singlet addition reaction. Therefore using a single determinant wave function, as found in Hartree−Fock self-consistent field (SCF) theory for example, is totally inadequate, even for a ground state potential surface of the addition reactions discussed above. Further supporting evidence comes from the fact that in a systematic study using two different basis sets and Møller−Plesset perturbations up to fourth order, it was found that the insertion barrier can only be predicted reliably by going beyond the SCF level.[6,36]

It is hoped that our study will provide a stimulation for further research into the subject.

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