Reactivity Scale for Sizeable Molecules

Hiroshi Fujimoto,* Kazuya Hatakeyama, Shinichi Kawasaki and Yasuo Oishi
Division of Molecular Engineering, Kyoto University, Kyoto 606, Japan

With a view to evaluating easily the reactivities of an atom or a functional unit in sizable molecules, we define a reactive orbital that is localized around the reaction site. We represent first the characteristics of a reaction by choosing a certain reference orbital function. Then, by projecting it onto the occupied or unoccupied MOs of a molecule, we can generate the reactive orbital that has the maximum amplitude on that reference orbital function. The occupied or unoccupied orbital obtained in this manner for a sizable molecular system interprets the local electron-donating or -accepting ability of an atom or a functional unit. A combination of local electrophilicity and nucleophilicity of the reagent and reactant molecules gives rise to a new reactivity scale. Applications to two types of reaction are shown to give excellent agreement with experimental results. The electronic effect of ligands on the catalytic activities of Pd complexes in the model Wacker process and the activation of a carbene upon co-ordination to transition metals are also discussed.

A recent trend in theoretical chemistry is to carry out accurate molecular orbital (MO) calculations on chemically reacting systems to determine the transition-state structures on the potential-energy surfaces and to estimate theoretically the height of the activation barrier.[1] These calculations are usually made for simplified reaction models. On the other hand, experiments are carried out on complicated systems to develop new processes. It is important, therefore, to have some ways of analysing and generalizing the results of calculations on the simplified models in order to get some insight into chemical interactions in more realistic systems. It is desirable to be able to predict relative reactivities of large molecules. The stereoselection rules of Woodward and Hoffmann have shown clearly that the phase relation between the frontier MOs is crucial for electrocyclic reactions to occur readily.[2] Hence, organic chemists discuss reaction mechanisms in terms of the symmetry of orbitals. This example indicates how important it is to clarify the factors which control the reactivity of molecules and the selectivity of reactions, even if one can locate the transition state on the potential surfaces by MO calculations. One of the purposes of theoretical calculations is to provide new insight into problems in chemistry.

Chemical interactions are local by nature. In reactions between sizable molecules, only a part of the reagent and a part of the reactant are actively involved in interactions. They are called 'reaction sites' or 'functional groups' in organic chemistry. Reactivity indices were derived in the 1940–50s by connecting the basic concepts in chemistry with the MO theory,[3–12] but these useful notions are no longer appropriately represented in conventional MO calculations on reacting systems. Recently, Parr and co-workers proposed a new reactivity index for π-electron systems by applying the density functional theory.[13] The barrier height of reactions seems to be controlled by several electronic and structural factors. Some of these indices were functions of the factors which should destabilize the reagent and reactant species, while some others were functions of the factors which should stabilize the reacting system as the measure of reactivity.

In a discussion of local interactions between molecules, the method of natural bond orbitals was applied.[14] For each bond, a bonding orbital is assigned by taking the in-phase linear combination of atomic hybrids of the two bound atoms. The out-of-phase combination of two hybrid AOs also contributes to the bond (to a minor extent), having a small electron population. Interactions between two molecules are discussed

in terms of these orbitals by applying perturbation treatment. Several years ago, we proposed a method of analysing the results of MO calculations on a composite reacting system by means of the pairs of interacting orbitals of the reagent and reactant.[15–17] These orbitals were found to be localized on an atom of each fragment species in a one-centre reaction, and were delocalized over several atoms in a multi-centre reaction. They could indicate what changes were going to take place in the reaction. In the protonation of a C=C double bond, for instance, a hexatriene molecule and a graphite-like large conjugated system yielded interacting orbitals that looked very similar to the highest occupied MO(HOMO) π of an ethylene molecule which makes orbital pairs with the 1s AO of the proton.[15b] In a model Diels–Alder cycloaddition between hexatriene and ethylene, on the other hand, the hexatriene molecule gave occupied and unoccupied interacting orbitals that bore close resemblances to the HOMO and the lowest unoccupied MO(LUMO) of butadiene, respectively.[15b] Molecules of different sizes and with different structures utilize similar orbitals for a given reaction, while a molecule generates different reactive orbitals for different types of reactions. This view of orbital interactions seems to provide us with a clue to understanding the common aspects and the variety of chemical reactions. We report in this paper a reactivity index which will be applied to single-centre and multi-centre reactions of sizable molecules in a unified manner. It is furnished with a concept of electron orbitals and is closely connected with the notion of 'functional groups' in chemistry.

Method

As mentioned above, our orbital analyses on reacting systems have demonstrated that chemical interactions are represented by a few pairs of fragment orbitals that are localized specifically in the functional units. The orbitals that participate in electron delocalization in a given type of reaction show close resemblance to each other for a variety of reagent and reactant.[15–17] In order to utilize this knowledge, we attempted to devise a scheme for obtaining such orbitals for isolated reactant molecules without performing time-consuming MO calculations on the whole reacting systems.[18]

We define first a reference orbital δ_r. This orbital function should have its amplitude within a certain functional group and an appropriate nodal property to specify the reaction processes. It is given either by an AO χ_s or by a linear combination of the

AOs. The reference function is expanded in terms of the occupied and unoccupied canonical MOs of a reactant molecule that contains that structural unit, as shown in eqn. (1).

$$\delta_r = \sum_s b_{s,r}\chi_s$$

$$= \sum_i^{oc} d_{i,r}\varphi_i + \sum_j^{unoc} d_{j,r}\varphi_j \qquad (1)$$

By using the coefficients $d_{i,r}$ and $d_{j,r}$, one can determine the occupied and unoccupied orbitals that have the maximum amplitude on δ_r. The projected occupied orbital φ_{oc}' is given by a linear combination of the occupied canonical MOs φ_i, and the unoccupied orbital φ_{unoc}' is given by a combination of the unoccupied canonical MOs φ_j of the molecule. The local electron-donating or -accepting strength of the structural unit in that molecule is evaluated by taking the sum of the orbital energy of the constituent MO[18] [eqns. (2) and (3)] where ε_k signifies the orbital energy of φ_k.

$$\lambda_{oc}(\delta_r) = \sum_i^{oc} d_{i,r}^2 \varepsilon_i \bigg/ \left(\sum_i^{oc} d_{i,r}^2 \right) \qquad (2)$$

$$\lambda_{unoc}(\delta_r) = \sum_j^{unoc} d_{j,r}^2 \varepsilon_j \bigg/ \left(\sum_j^{unoc} d_{j,r}^2 \right) \qquad (3)$$

When we use the MO methods which neglect overlap integrals, e.g., simple Hückel, MNDO,[19] and so on, the co-efficient $d_{i,s}$ is replaced by the LCAO MO coefficient $c_{s,i}$ for a single-centre reaction at an AO χ_s. For an electrophilic reaction, we have eqns. (4) and (5) where q_s and $P_{s,t}$ are the electron

$$\bar{\varphi}_{oc}' = [(q_s)^{\frac{1}{2}}/\sqrt{2}]\chi_s + \sum_{t \neq s} [P_{s,t}/(2q_s)^{\frac{1}{2}}]\chi_t \qquad (4)$$

$$\lambda_{oc} = \sum_{i=1}^m 2c_{s,i}^2 \varepsilon_i/q_s \qquad (5)$$

density of χ_s and the bond order between χ_s and χ_t. It is shown in equation (4) that electron density is donated mainly from the reaction centre s to the reagent electrophile. The nearby atoms, t, also donate electronic charge. The bonds are loosened between the reaction centre and the neighbouring atoms for which $P_{s,t}$ has significant values. Eqn. (5) indicates that the local electron-donating strength of the reaction centre s should be larger when the electron density of the reaction centre is populated more heavily in the higher lying occupied MOs. This simple example shows that our present treatment gives a natural description of chemical interactions.

Now, by denoting the electron-donating and -accepting abilities of a reagent A by λ_{Aoc} and λ_{Aunoc}, respectively, and those of a reactant molecule B by λ_{Boc} and λ_{Bunoc}, respectively, a reactivity index may be defined by eqn. (6). The first term on the

Reactivity Index $= 1/(\lambda_{Aunoc} - \lambda_{Boc}) + 1/(\lambda_{Bunoc} - \lambda_{Aoc})$ (6)

right-hand side estimates the magnitude of electron delocalization from B to A and the second term measures that from A to B. We may include in eqn. (6) the overlap between the reactive orbitals of A and B in order to evaluate the extent of localization of the interaction around the reaction sites. It was found, however, that replacement of the numerator by the square of the overlap integral did not improve significantly the correlation with experimental results.

We consider here a case in which A plays the electron-donor part and B the electron-acceptor part. The activation barrier

will be lower as the stabilization due to electron delocalization gets larger. The magnitude of stabilization is proportional to $1/(\lambda_{Aoc} - \lambda_{Bunoc})$ (< 0). The effect of a substituent group of B upon the reaction rate k is then estimated by eqn. (7) where k_0

$$\log(k/k_0) \propto 1/(\lambda_{Aoc} - \lambda_{Bunoc}) - 1/(\lambda_{Aoc} - \lambda_{Bunoc}^0)$$
$$= (\lambda_{Bunoc} - \lambda_{Bunoc}^0)/(\lambda_{Aoc} - \lambda_{Bunoc})(\lambda_{Aoc} - \lambda_{Bunoc}^0)$$
$$\cong (\lambda_{Bunoc} - \lambda_{Bunoc}^0)/(\lambda_{Aoc} - \lambda_{Bunoc}^0)^2 \qquad (7)$$

and λ_{Bunoc}^0 are for B without any substituent group. The numerator shows the change in the level of the unoccupied reactive orbital of B due to the introduction of a substituent group and has been demonstrated to give an excellent correlation with Hammett σ-values for substituted benzene molecules.[18,20] The denominator is given by the square of the gap between the levels of φ_{oc}' of A and φ_{unoc}' of B. It indicates how sensitive the reaction will be to the substituent groups introduced in B. A similar discussion holds for the case in which A plays the electron-acceptor part and B the electron-donor part. The numerator $(\lambda_{Boc}^0 - \lambda_{Boc})$ is close in magnitude to $(\lambda_{Bunoc} - \lambda_{Bunoc}^0)$ for a given substituent, but opposite in sign.[18] We may now define another index which specifies the type of reaction by equation (8).

Reaction Index $= 1/(\lambda_{Aoc} - \lambda_{Bunoc}^0)^2 -$
$$1/(\lambda_{Boc}^0 - \lambda_{Aunoc})^2 \qquad (8)$$

To obtain a good scale for the local electron-donating or -accepting abilities for sizable systems, we should choose a good reference function which specifies the chemical interaction involved in a given reaction. The choice of the function for single-centre interactions is rather straightforward. As for multi-centre reactions, our analyses of reacting systems by the paired interacting orbital method as mentioned above suggest that the frontier orbital of the smallest molecule that involves the same functional unit serves as a good reference function.[15] For instance, the HOMO of an ethylene unit can be taken as the reference function in discussing the reactivities of a C=C bond in large conjugated species against an electrophile.

Results and Discussion

Additions of Radicals to Alkenes.—As an application of indices, we examine first the reactivities of free-radicals. The transition-state structures have been determined by *ab initio* MO calculations for the addition of a hydrogen atom,[21,22] and of the radicals centred on carbon and oxygen atoms to unsaturated bonds.[23,24] Free radicals have both electron-attracting and -donating properties. Our orbital analyses of the interactions between a radical and a closed-shell molecule showed that the bonding and chain-transfer in radical reactions were governed by electron delocalization and the associated spin-polarization within each of the two species.[16a,25] In the frontier orbital theory, they are represented approximately by the singly occupied MO (SOMO) of a radical and the HOMO and the LUMO of a reactant closed-shell molecule.[9,25b] In the present treatment of sizable species, we project out the singly occupied and unoccupied reactive orbitals that have the maximum amplitude around the reaction centre. Electrostatic interactions are usually not so strong in radical reactions as in ionic reactions.

A reaction taken here is the addition of thiyl radicals to olefins.[26] The MOs of the radicals were calculated by the unrestricted open-shell method with the minimal basis STO-3G basis set.[27] The C–S bond distance was taken to be 0.18 nm and standard values were taken for other geometrical parameters. In order to estimate the local electron-donating and -accepting abilities of those radicals at the reaction centre, we have chosen

Table 1 Levels of occupied and unoccupied reactive orbitals of thiyl radicals and alkenes (in au)
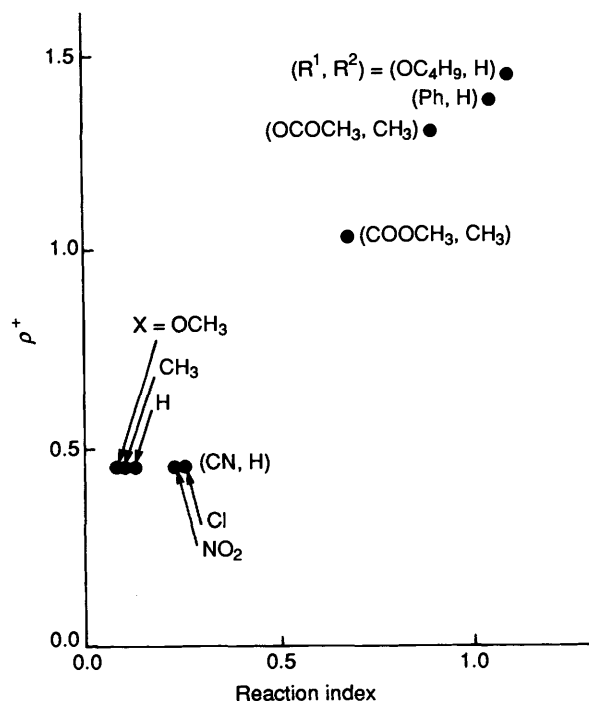
Thiyl radical			Alkene		
X	λ_{Roc}	λ_{Runoc}	R^1, R^2	λ_{Ooc}	λ_{Ounoc}
H	−0.346	0.222	Ph, H	−0.325	0.313
Me	−0.343	0.225	CN, H	−0.374	0.262
Cl	−0.358	0.210	CO_2Me, Me	−0.344	0.294
OMe	−0.345	0.228	OAc, H	−0.341	0.317
NO_2	−0.360	0.207	OBu, H	−0.329	0.326
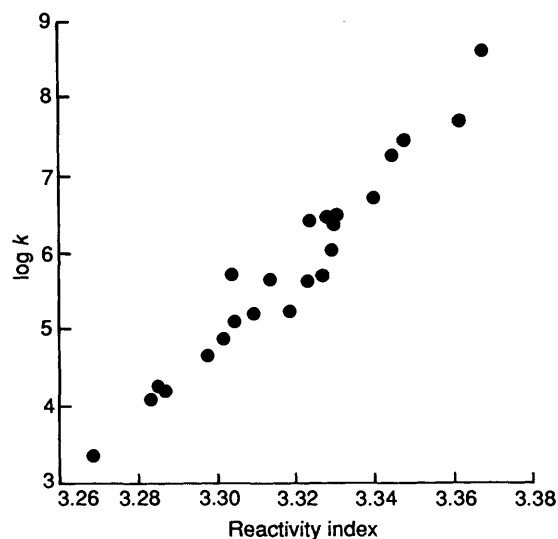
Fig. 1 Correlation between the Reactivity Index and the observed reaction rate for the addition of thiyl radicals to carbon–carbon double bonds

the $3p_\pi$ AO of the sulphur as the reference function δ_r. The MOs of alkene molecules were calculated by the usual restricted Hartree–Fock method with the same basis set and the $2p_\pi$ AO of the C_1 atom was chosen as the reference function. Incidentally, projection of a carbon $2p_\pi$ AO onto the occupied and unoccupied MO spaces of an ethylene molecule gives rise to the π and π^* MOs, respectively. Our previous analysis of the protonation of formaldehyde and furan by paired interacting

R^1	R^2
H	OC_4H_9
H	Ph
H	$OCOCH_3$
CO_2CH_3	CH_3
H	CN

X = H, CH_3, Cl, OC_4H_9, NO_2
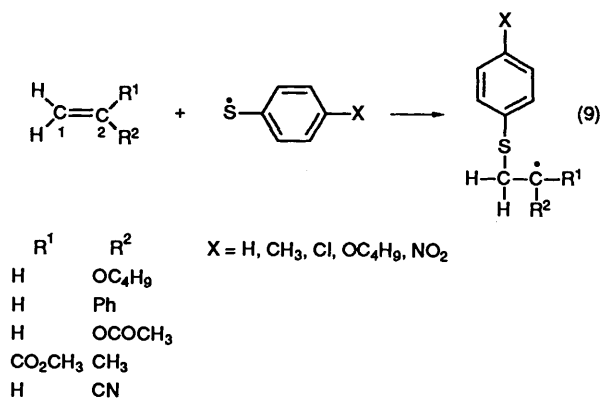
orbitals showed that the larger basis set, 4-31G and 6-31G**, produced additional orbital pairs that should contribute weakly to the bonding. The major orbital pair was found to be very similar to that obtained for the minimal basis set.[15b] With respect to the electrophilic addition of singlet carbenes, 6-31G** calculations gave the same reactivity trend as that obtained by

Fig. 2 Correlation between the Reaction Index and the Hammett ρ^+ value for the addition of thiyl radicals to carbon–carbon double bonds

the calculation with the minimal basis set.[28] Arguments based on a simple orbital interaction scheme and calculations with a small basis set will be useful for the prediction of experimental results.

The five radicals in eqn. (9) have been shown to give reactive orbitals almost the same in shape. The five alkenes have given the occupied and unoccupied reactive orbitals which look similar to the π and π^* MO of an ethylene molecule, respectively. Table 1 summarizes the λ-values of phenylthiyl radicals and of the alkene molecules. With these λ-values, the Reactivity Index was calculated by using eqn. (6), as presented in Fig. 1. One sees an excellent correlation between the index and the logarithm of experimentally observed rate constant k for the 25 combinations of radicals and C=C bonds. Vinyl acetate gives the smallest values of index among the C=C compounds, while styrene shows the largest values, in agreement with experimental observation. Among the five radicals, the reactivity is shown to increase in the order of $OCH_3 < CH_3 < H < Cl < NO_2$, also in agreement with experiments.

The first and second terms in eqn. (6) give values that are almost the same in magnitude in the cases of $(R^1, R^2) = (CN, H)$ and $X = OCH_3$ and CH_3. In other combinations, the second term is larger than the first term, indicating that the radicals act as electron acceptors. Fig. 2 presents a relation between the Reaction Index defined above and the Hammett ρ^+ -value determined experimentally.[26] It is suggested in eqn. (7) that the denominator should also include an effect due to the substituent groups in the radical. Fig. 2 shows, however, that this effect is not significant for $(R^1, R^2) = (CN, H)$. A similar result was obtained for other C=C compounds. Thus, by utilizing the reactive orbitals, one can predict easily in which manner and to what extent a reaction will be influenced by the substituent groups.

Ozonation of Alkenes.—A similar argument applies also to multi-centre reactions. Fig. 3 shows the relationship between the rate of ozonation of several electron-deficient alkenes[29] and the Reactivity Index calculated by STO-3G calculations.[27] Here, the O–O bond length was taken to be 0.128 nm and the O–O–O

$$O_3 + \quad \begin{matrix} R^1 \\ R^2 \end{matrix} C{=}C \begin{matrix} R^3 \\ R^4 \end{matrix} \quad \longrightarrow \quad R^1{-}C{-}C{-}R^3 \quad (10)$$
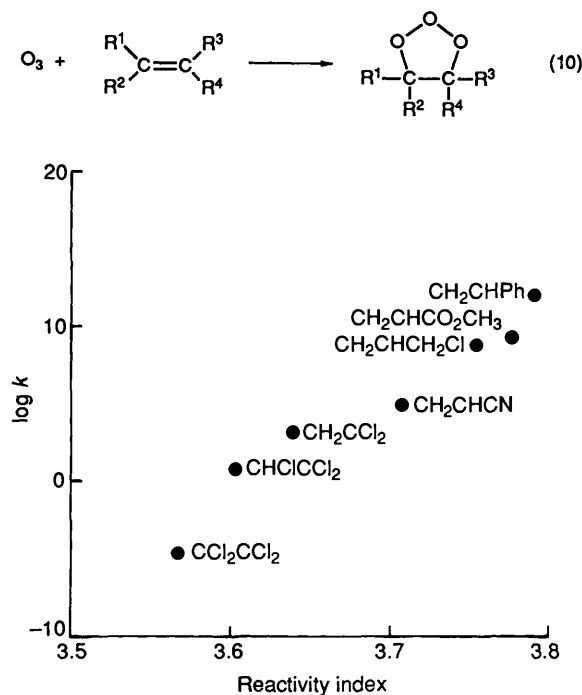
Fig. 3 Correlation between the Reactivity Index and the reaction rate for the ozonation of alkenes
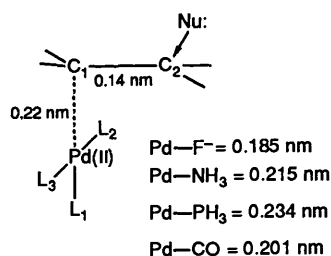
Fig. 4 A sketch of the reaction model for nucleophilic additions to a C=C bond

Pd—F⁻ = 0.185 nm
Pd—NH₃ = 0.215 nm
Pd—PH₃ = 0.234 nm
Pd—CO = 0.201 nm

Table 2 Changes in the level of unoccupied reactive orbital of an ethylene molecule co-ordinated to Pd complexes

L_1	L_2	L_3	λ/au
F⁻	F⁻	F⁻	0.3918
NH₃	F⁻	F⁻	0.2385
PH₃	F⁻	F⁻	0.2380
CO	F⁻	F⁻	0.2232
NH₃	NH₃	F⁻	0.0668

angle 117°. The π and π^* MOs of a C=C bond unit were chosen as the reference functions and were projected onto the occupied and unoccupied MO subspaces of the alkenes, respectively. For an ozone molecule, the out-of-phase and in-phase combinations of the p_π AOs of two terminal oxygen atoms were taken as the references, by assuming that the reaction was concerted. These orbital functions generated the π_2 and π_3 canonical MOs as the occupied and unoccupied reactive orbitals. Their levels were -0.323 and 0.100 au. Ozone is the smallest and symmetric molecule that undergoes addition of the type as sketched in eqn. (10). Our reactive orbitals are nothing but the frontier orbitals in such a case, as mentioned above. A good agreement was obtained between the rate and the theoretical reactivity scale, as illustrated in Fig. 3. In the case of CCl₂=CCl₂, the levels of the occupied and unoccupied reactive orbitals were calculated to be -0.501 au and 0.204 au, respectively. The gap between the

levels of the occupied orbital of ozone and the unoccupied reactive orbital of CCl₂=CCl₂ is smaller than that between the unoccupied orbital of ozone and the occupied reactive orbital of the alkene. This suggests that CCl₂=CCl₂ acts as the electron acceptor. In CH₂=CCl₂, the donor–acceptor relation is reversed. It gives occupied and unoccupied reactive orbitals of -0.425 and 0.254 au, respectively.

With respect to cycloadditions, there has been controversy concerning the mechanism. The cycloaddition between ethylene and butadiene, for instance, was suggested to be concerted from the orbital symmetry viewpoint.[2] A recent calculation showed that it could be concerted and synchronous, although a previous study preferred the two-step biradical mechanism.[30] We calculated the reactivity scale for the one-centre interaction between an ozone molecule and an alkene molecule by taking the $2p_\pi$ AO of one of the terminal oxygens of ozone and the $2p_\pi$ AO of each carbon in the alkene as the reference orbitals. The agreement with experimental results turned out to be worse.

Activation of Molecules by Transition-metal Complexes.—We look next at how catalysts can activate organic molecules: consider the model illustrated in Fig. 4. The driving force of this reaction is electron delocalization from the attacking nucleophile to the unoccupied MOs of the ethylene molecule co-ordinated to the catalyst. By taking the p_π AO of C_2 as the reference orbital, we can project out the unoccupied orbital that bears a resemblance to the π^* MO of an ethylene molecule in its nodal property. The orbitals obtained here are localized on the C=C bond, the contribution of C_2 p_π AO being estimated to be *ca.* 65% by Mulliken population analysis,[31] though the LUMOs are delocalized over the constituent AOs of the whole system.[32,33] The formation of a new bond between the ethylene C_2 and the attacking nucleophile and the breaking of the C_1–C_2 π bond upon accepetance of an electron from the nucleophile can be represented appropriately by this unoccupied reactive orbital. The calculated value of λ_{unoc} is listed in Table 2. Here, Huzinaga's basis set [15s, 10p, 6d]/(5s, 4p, 2d) combined with a p-type polarization function (α 0.091) was adopted for Pd.[34]

It is seen that the co-ordination to Pd complexes with neutral ligands (NH₃, PH₃ or CO) yields a low lying, unoccupied, reactive orbital, indicating that the reactivity of the C=C bond is enhanced. This is in agreement with experimental findings that Pdᴵᴵ complexes with electron-withdrawing ligands efficiently catalyse additions of nucleophiles to C=C bonds.[35,36]

Carbenes in Fisher-type complexes are known to react with carbanions, amines, and sulphur compounds to give other carbene complexes.[37] We therefore studied the reactivity of CH(OH) co-ordinated to Ni⁰, Cr⁰ and Fe⁰ as illustrated in Fig. 5. The Fe–C, Cr–C and Ni–C distances were taken to be 0.20, 0.20[38] and 0.19 nm[39] for the carbene ligand and 0.18 (Fe–CO_ap), 0.184 (Fe–CO_eq),[40] 0.191[39] and 0.182 nm[41] for the C–O ligands. The carbene was fixed in a planar structure as shown in Fig. 5 and the standard values were taken for other geometrical parameters. Huzinaga's basis set [12s, 7p, 3d]/(4s, 3p, 1d) with a p-type polarization function was adopted for Fe (α 0.075), Ni (α 0.111) and Cr (α 0.086).[34] The local ability of carbene ligands to accept electrons, calculated by taking the 2p AO of C_1 as δ_r is given in Fig. 5. The reactivity of a carbene ligand against a nucleophile is predicted to be enhanced in the order $Fe_{eq} < Cr < Ni < Fe_{ap}$, provided that electron delocalization from an attacking nucleophile governs the reactions.

Chemical interactions are usually discussed from several different aspects, *e.g.* the electrostatic interaction, overlap repulsion, electron delocalization and so on.[42,43] However, so far as the reorganization of bonds is the major process of a reaction, as is often the case, delocalization of electrons should control the reaction path.[44]
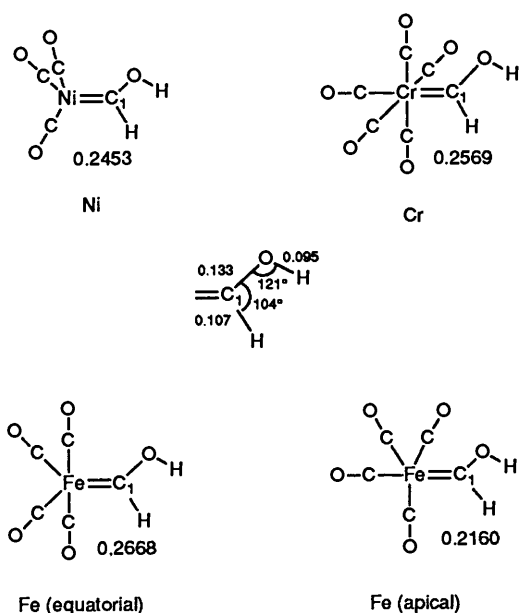
Fig. 5 A sketch of Fisher-type carbene complexes of Ni^0, Fe^0 and Cr^0 and λ_{unoc}-values of the orbital having the maximum amplitude on C_1. Distances are in nm.

We have shown above that our chemical reactivity scale based on electron delocalization gives excellent agreement with the experimental results. In deriving the indices, we have utilized our knowledge obtained from our previous analyses of the results of MO calculations on reacting systems. The present approach may be used in any scheme of MO calculations, having a potential applicability for any type of reaction by devising an approximate reference orbital.

Sophisticated theoretical calculations can interpret or predict chemical reactions, but they are not often so useful in the day-to-day routine of experimental chemists. The frontier orbital theory is utilized as a simple theoretical method that works for a variety of organic reactions. When we deal with reactions of large molecular systems the treatment presented here, to elucidate the local behaviour of functional groups or structural units, makes it possible to connect theoretical calculations with our intuition based on the familiar concepts of chemistry, e.g., bonds, reactions sites and the electronegativity of atoms or groups. Information concerning relative reactivities of a functional group in different molecules or different positions in a molecule will be of use in predicting the products in new reaction processes. An extension towards analysis of the selectivities in terms of the spatial direction of the attack of reagents is in progress.

Acknowledgements

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