Theoretical Study of the Dependence on Substrate of the Reactivity of Carbenes

Miguel Moreno, José M. Lluch, Antonio Oliva, and Juan Bertran *
Departament Química Física, Universitat Autonoma de Barcelona, Bellaterra, Barcelona, Spain

The transition states for the addition of $C(OH)_2$ and $C(NH_2)_2$ to ethylene, hydroxyethylene, and acrolein have been located, using the STO-3G basis set, in order to examine the philicity of both carbenes. It is shown that $C(NH_2)_2$ can be classified as a nucleophile and $C(OH)_2$ as an ambiphile. The degree of validity of this classification is discussed.

A carbene selectivity scale has been obtained from the relative reactivity toward a standard set of alkenes.[1–3] Depending on its position on this scale, carbenes can be classified as electrophiles, nucleophiles, or ambiphiles. The electrophiles exhibit steadily decreasing reactivity as the alkene changes from electron-rich to electron-poor. On the contrary, the addition of nucleophilic carbenes is facilitated by placing electron-attracting groups on the alkene carbons. Finally, ambiphilic carbenes act as electrophiles toward electron-rich alkenes and as nucleophiles toward electron-poor alkenes, in such a way that their reactivity increases by placing both electron-donating or electron-withdrawing groups on the alkene carbons.[4,5]

This classification of carbenes is easily understood in terms of frontier molecular orbital interactions.[6,7] In the addition of electrophiles, the dominant orbital interaction is that between the LUMO of carbene and the HOMO of alkene, thus leading to charge transfer from alkene to carbene. On the other hand, the interaction between the HOMO of carbene and the LUMO of alkene is dominant in the addition of nucleophiles, charge transfer now being directed in the opposite sense. Finally, in the case of ambiphilic carbenes both HOMO–LUMO interactions are very similar and it is obvious that substitution of electron-donating or electron-withdrawing groups on the alkene can easily lead to one of the above mentioned situations.

The case of nucleophilic carbenes is of special theoretical interest since few experimental data for their reactivity are known.[8] In particular, $C(OH)_2$ and $C(NH_2)_2$ are situated in the nucleophilic zone of the selectivity scale,[4] but some controversy has arisen about its nucleophilic character. MNDO calculations[9] for the addition of both carbenes to ethylene, 1,1-dihydroxyethylene, and 1,1-difluoroethylene have shown clear nucleophilic behaviour. However, *ab initio* frontier orbital calculations[7] seem to indicate that $C(OH)_2$ will act as an ambiphile, since for $C(OCH_3)_2$, which is a very similar carbene, the dominant HOMO–LUMO interaction depends on the alkene being used.

The object of this work is to clarify the above mentioned controversy and to discuss the degree of validity of the nucleophilic character usually assigned to $C(OH)_2$ and $C(NH_2)_2$. This will be done by directly locating the transition states in the STO-3G reaction hypersurface for the additions of both carbenes to ethylene, hydroxyethylene, and acrolein.

Methods

Ab initio calculations were done with the GAUSSIAN 80 series of programs,[10] using a minimal STO-3G basis set.[11] This basis set has been chosen in order to keep the volume of calculations within reasonable limits, since the introduction of substituents on methylene and ethylene noticeably increases the size of the system and a comparative study of all the reactions with more extended basis sets becomes impractical for economic reasons. The transition states have been directly located in the complete potential hypersurface using the Schlegel algorithm[12] for gradient minimization.

Table 1. Energy barriers (kcal mol^{-1})

Carbene	Hydroxyethylene Subst. C atom	 Unsubst. C atom	Ethylene	Acrolein Subst. C atom	 Unsubst. C atom
$C(NH_2)_2$	34.1	38.8	32.6	36.8	18.2
$C(OH)_2$	33.3	28.9	30.6	35.6	21.0

Results and Discussion

There exist four possible ways carbenes can approach the substituted carbon atom of the alkene. Previously[13] we have calculated the potential surfaces corresponding to these four types of approach for the addition of singlet methylene to hydroxyethylene and acrolein. We have shown that only the 'inward' approaches lead to the addition reaction, 'outward' approaches leading to the insertion of methylene in a C–H bond of the alkene. For this reason, in the present paper, we have located the stationary points with only one negative eigenvalue corresponding to the 'inward' approaches of $C(OH)_2$ and $C(NH_2)_2$ to hydroxyethylene, ethylene, and acrolein. The energy barriers for these stationary points are presented in Table 1.

In the addition to hydroxyethylene and acrolein, there are two stationary points with only one negative eigenvalue which correspond to the 'inward' approaches to the substituted and the unsubstituted carbon atom of the alkene, respectively. According to McIver and Komornicki's conditions[14] the transition state is that corresponding to the minor energy barrier. So, while the most favourable approach of $C(OH)_2$ is always to the unsubstituted carbon atom of the alkene, $C(NH_2)_2$ approaches the unsubstituted carbon atom in the addition to acrolein, but the substituted carbon atom in the addition to hydroxyethylene.

Let us now study the nucleophilic or ambiphilic character of both carbenes. From the results presented in Table 1, one can observe that $C(NH_2)_2$ has clear nucleophilic character, since the energy barrier increases insofar as the alkene is more electron-rich. On the contrary, $C(OH)_2$ acts as an ambiphile, since the energy barrier decreases when electron-donating or electron-withdrawing substituents are introduced in the ethylene.

As mentioned in the Introduction the behaviour of both carbenes and the values of the energy barriers can be rationalized in terms of frontier orbital interactions. Table 2 presents the calculated HOMO–LUMO energy differences for

Table 2. HOMO–LUMO Energy differences (eV)

	$C(OH)_2$		$C(NH_2)_2$	
Alkene	p–Π[a]	Π*–σ[b]	p–Π[a]	Π*–σ[b]
$CH_2{=}CH(OH)$	16.05	16.82	17.06	16.27
$CH_2{=}CH_2$	17.37	16.65	19.20	16.14
$CH_2CH(CHO)$	17.14	13.99	18.97	13.44

[a] E_{LUMO} carbene–E_{HOMO} alkene. [b] E_{LUMO} alkene–E_{HOMO} carbene.

Table 3. Frontier orbital coefficients on the alkene carbons

	Hydroxyethylene		Acrolein	
	Unsubst. C atom	Subst. C atom	Unsubst. C atom	Subst. C atom
HOMO	0.64	0.44	0.58	0.56
LUMO	0.77	0.84	0.61	0.42

the additions of $C(OH)_2$ and $C(NH_2)_2$ to hydroxyethylene, ethylene, and acrolein. In the case of $C(NH_2)_2$ one can observe that the dominant interaction is always that between the HOMO of the carbene and the LUMO of the alkene, the difference between both orbitals steadily increasing as far as the alkene becomes more electron-rich. This explains the similar trend followed by the energy barrier of the addition which is a maximum in the case of hydroxyethylene.

For $C(OH)_2$ the interaction between the HOMO of the carbene and the LUMO of the alkene is also dominant for the additions to acrolein and ethylene, but the other HOMO–LUMO interaction is more important when this carbene adds to hydroxyethylene. The fact that the dominant interaction changes and the values of the corresponding HOMO–LUMO energy differences permit a prediction that $C(OH)_2$ will act as an ambiphile and that the greatest energy barrier will be for the addition to ethylene, predictions which clearly agree with the results presented in Table 1.

Frontier orbital considerations permit an understanding of which carbon atom of the alkene is initially attacked by the carbene. According to these considerations it is well known that carbenes will preferentially attack the alkene carbon atom where the frontier orbital which intervenes in the dominant HOMO–LUMO interaction has the greatest coefficient. Table 3 presents the coefficients for both alkene carbons for the frontier orbitals of hydroxyethyelene and acrolein. In the additions of $C(NH_2)_2$ to both alkenes, it is always the LUMO of alkene which intervenes in the dominant frontier orbital interaction. The values of the coefficients of the LUMO orbitals predict that $C(NH_2)_2$ will approach the unsubstituted carbon of acrolein, but the substituted one in the addition to hydroxyethylene. The situation is not the same for $C(OH)_2$, since, as mentioned in the preceding paragraph, the dominant HOMO–LUMO interaction changes when one goes from hydroxyethylene to acrolein. So, one has to consider the LUMO coefficients of acrolein, but the HOMO coefficients of hydroxyethylene. In this way, frontier orbital considerations predict that $C(OH)_2$ will initially approach the unsubstituted carbon atom of both alkenes. All these predictions are in good agreement with the energy barriers obtained in this work which we presented in Table 1.

To gain a deeper insight into the nucleophilic or ambiphilic character of both carbenes, Table 4 presents the main geometrical parameters (see Figure 1) and the charge transfer for the transition states corresponding to their additions to hydroxyethylene, ethylene, and acrolein.*

Table 4. Main geometrical parameters and charge transfer for the transition states of the additions of $C(NH_2)_2$ and $C(OH)_2$

	$C(NH_2)_2$			$C(OH)_2$		
	Hydroxy-ethylene	Ethylene	Acrolein	Hydroxy-ethylene	Ethylene	Acrolein
r_1[a]	2.26	1.80	1.90	1.78	1.78	1.83
r_2[a]	1.81	2.31	2.59	2.21	2.24	2.44
α[b]	59.2	61.2	87.2	34.2	49.2	57.6
c.t.[c]	−0.069	−0.092	−0.233	0.106	0.002	−0.143

[a] In Å. [b] In degrees. [c] Charge transfer in a.u., positive when directed towards the carbene.

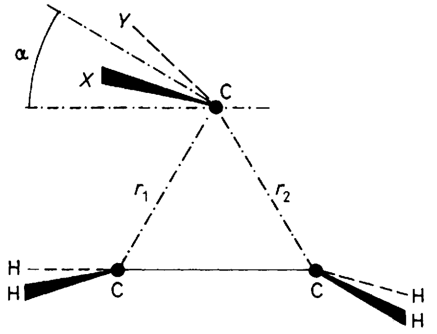

Figure 1. Important geometrical parameters for the addition reaction of carbenes to alkenes

The angle α is specially significant, since it has been taken as an indicator of carbene philicity. According to Moss,[7] for the addition of electrophiles to ethylene α < 45°, for nucleophiles α > 50° and the intermediate values correspond to ambiphiles. It is interesting to observe that the values of α obtained in our work for the additions to ethylene are in good agreement with the nucleophilic and ambiphilic character of $C(NH_2)$ and $C(OH)_2$, respectively. It is also remarkable that the values of α for the addition of $C(NH_2)_2$ are always > 50°, α increasing when the alkene becomes more electron-rich. This variation of α is also observed for $C(OH)_2$ but now, its values clearly correspond to the electrophilic zone of Moss classification for the addition to hydroxyethylene and to the nucleophilic zone for the addition to acrolein.

In Table 4 one can also observe a good correlation between the philicity of the carbene and the sense of the charge transfer in the transition state, this charge transfer being directed to the carbene or to the alkene when the carbene acts as an electrophile or a nucleophile, respectively.

In fact the relationship between the angle α, the charge transfer, and the philicity of the carbenes is not so difficult to understand if one takes into account that the relative orientation of both reactants will tend to increase the dominant HOMO–LUMO interaction. It is well known that the HOMO of the carbene is situated in the molecular plane and that the LUMO is perpendicular to this plane. So, when the carbene acts as a nucleophile, α must be large in order to permit good overlap between the HOMO of the carbene and the LUMO of the alkene. Charge transfer will then be directed to the alkene, its value increasing as far as the approach is more perpendicular. On the contrary, when the carbene acts as an electrophile, α

---

* The complete geometries of the transition states are available from the authors upon request.

must be small in order to increase the overlap between the other pair of frontier orbitals whose interaction is now dominant and the charge transfer will now be directed to the carbene.

All the arguments used in this work in order to discuss the philicity of the carbenes show that $C(NH_2)_2$ is a clear nucleophile and $C(OH)_2$ is an ambiphile. However, an important remark about the degree of validity of this classification must be done. In Table 2 one observes that the two HOMO–LUMO energy differences for the addition of $C(NH_2)_2$ steadily approach one another insofar as the alkene becomes more electron-rich. It is possible that the dominant HOMO–LUMO interaction could change provided that an alkene more electron-rich than hydroxyethylene is used. This possibility has been investigated by calculating the STO-3G HOMO–LUMO energy differences corresponding to the addition of $C(NH_2)_2$ to tetrahydroxyethylene. It has been found that these energy differences are 16.29 and 16.42 eV, the minor value corresponding to the energy difference between the LUMO of the carbene and the HOMO of the alkene. So, frontier orbital theory predicts that in this case $C(NH_2)_2$ will act as a soft electrophile, thus putting in question the nucleophilic character usually attributed to this carbene.

Conclusions

In spite of the limitations of the STO-3G basis set which prevent quantitative conclusions being obtained, the results clearly show that the philicity of carbenes depends on the set of alkenes which are used. While we have found that $C(NH_2)_2$ is a nucleophile and $C(OH)_2$ is an ambiphile with respect to the three alkenes considered in this paper, it is clear that the philicity of both carbenes may be different with respect to a different set of alkenes. So, the reactivity scale permits a definition of the relative philicity of carbenes but absolute philicity is a meaningless concept.

References

1 R. A. Moss and Ch. B. Mallon, *J. Am. Chem. Soc.*, 1975, **97**, 344.
2 R. A. Moss, Ch. B. Mallon, and Chi-Tang Ho, *J. Am. Chem. Soc.*, 1977, **99**, 4105.
3 N. G. Rondan, K. N. Houk, and R. A. Moss, *J. Am. Chem. Soc.*, 1980, **102**, 1770.
4 R. A. Moss and R. C. Munjal, *Tetrahedron Lett.*, 1979, 4721.
5 R. A. Moss, M. Fedorynski, and Wen-Chung Shieh, *J. Am. Chem. Soc.*, 1979, **101**, 4736.
6 W. W. Schoeller, *Tetrahedron Lett.*, 1980, **21**, 1505, 1509.
7 R. A. Moss, *Acc. Chem. Res.*, 1980, **13**, 58.
8 R. W. Hoffmann, W. Lillienblu, and B. Dittrich, *Chem. Ber.*, 1974, **107**, 3395; R. W. Hoffmann and M. Reiffen, *ibid.*, 1976, **109**, 2565; M. Reiffen and R. W. Hoffmann, *ibid.*, 1977, **110**, 37.
9 W. W. Schoeller, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 698.
10 J. S. Binkley, R. A. Whiteside, R. Khrishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, QCPE, 1980, **13**, 406.
11 W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657.
12 H. B. Schlegel, *J. Comput. Chem.*, 1982, **3**, 214.
13 M. Moreno, J. M. Lluch, A. Oliva, and J. Bertrán, *J. Chem. Soc., Perkin Trans. 2*, 1985, 131.
14 J. W. McIver and A. Komornicki, *J. Am. Chem. Soc.*, 1972, **94**, 2625.

Received 15*th April* 1985; *Paper* 5/628