ELSEVIER

Effect of electron-withdrawing substituents on the electrophilicity of carbonyl carbons

R. Contreras,[a,b,†,*] J. Andrés,[b,*] L. R. Domingo,[c,*] R. Castillo[b] and P. Pérez[d]

[a]*Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile*
[b]*Departament de Cienciès Experimentals, Universitat Jaume I, Box 224, 12080 Castelló, Spain*
[c]*Instituto de Ciencia Molecular, Departamento de Química Orgánica, Universidad de Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain*
[d]*Departamento de Ciencias Químicas, Facultad de Ecología y Recursos Naturales, Universidad Andrés Bello, República 275, Santiago, Chile*

Abstract—The substituent effects on the carbonyl carbon atom for a series of twelve substituted phenyl acetates have been rationalized using a global electrophilicity index. This index is linearly correlated with the experimental reaction rate coefficients. We found that, in contrast to the proposed interpretation based on experimental ^{13}C NMR chemical shifts and ground state destabilization calculations, the electrophilicity of carbonyl compounds increases due to the effect promoted by electron-withdrawing groups in these systems.
© 2004 Elsevier Ltd. All rights reserved.

1. Introduction

It is well established that nucleophilic attack on the carbonyl carbon of RCOX compounds depends mainly on the electron-withdrawing (EW) ability of both R and X substituents. The presence of an EW substituent in the leaving group, X, or in the remaining acyl group, R, increases the reaction rate coefficient.[1–3] This result has been confirmed by a Hammett analysis of the substituent constants, showing positive slopes when plotted against the reaction rate coefficients k.[2,3] This behavior has been currently interpreted as an increase in electrophilicity at the reaction center due to the presence of EW substituent in the carbonyl substrate.

The electrophilicity of the carbonyl carbon is one of the determining factors of the chemical reactivity exhibited by fundamental compounds, such as aldehydes, ketones or carboxylic acid derivatives. The substituent effects on nucleophilic reactions of acyl-substituted phenyl acetates and phenyl-substituted phenyl acetates have been studied recently by Neuvonen et al.[4,5] Good correlations with

negative slopes for the plots of log k versus the ^{13}C NMR chemical shift δ_C (C=O) have been found. The upfield shift of the carbonyl carbon signal in the ^{13}C NMR spectra was related with the EW ability of the phenyl substituent of phenyl dichloroacetates or benzoyl substituent in methyl benzoates.[4,5] Since an upfield chemical shift is usually associated with an increase of the electron density at the site, Neuvonen et al. interpreted this positive variation of the electron density at the carbonyl carbon as a decrease of the electrophilicity at this site.

Murray et al.[6] studied the reactivity of a series of cyclic ureides toward nucleophilic attacks, using the molecular electrostatic potential surface (MEPS) at the carbonyl carbon. For a series of substituted 2-imidazolidinones they found that the MEPS at the carbonyl carbon provided a basis for predicting the relative hydrolytic tendency. Susceptibility toward hydrolysis is expected to increase roughly as the MEPS becomes more positive. They also found that the calculated atomic charges at the carbonyl carbon bear little or no relationship to the electrostatic potential values.

Recently, we have shown[7–12] that the electrophilicity of a molecule may be conveniently described by the global index, ω, proposed by Parr et al.[13] This index, which measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment, is defined by the following simple

expression:[13]

$$\omega = \frac{\mu^2}{2\eta},\qquad(1)$$

in terms of the electronic chemical potential, μ (the negative of electronegativity), and the chemical hardness, η. Both quantities may be approached in terms of the one electron energies of the frontier molecular orbitals, HOMO and LUMO, ε_H and ε_L, as $\mu = (\varepsilon_H + \varepsilon_L)/2$ and $\eta \approx \varepsilon_L - \varepsilon_H$, respectively.[14]

Electrophilicity, as ranked in terms of reaction rates becomes a kinetic concept.[15] However, although there is no rigorous procedure to establish the kinetic character of the theoretical ω index, yet the comparison between both the experimental and theoretical electrophilicity scales[7,8] seems to confirm the ω index as a reliable quantitative representation of electrophilicity. According to Eq. 1, this index contains information about the propensity of the electrophile to acquire an additional electronic charge represented by the square of the electronegativity, and the resistance of the system to exchange electronic charge with the environment described by η. The atomic electron population, is in this sense, just a piece of information encompassed in the electrophilicity concept.

Substituent effects on electrophilicity evaluated from ω for Diels–Alder[9] and 1,3-dipolar cycloaddition[10] reactions have been found to be in good agreement with the experimental relative rates. Furthermore, it was found that the difference in electrophilicity for the diene/dienophile pair determined the nature of the reaction mechanism (non-polar or polar character of the process),[9] thereby reinforcing the reliability of the ω index as a kinetic descriptor of reactivity. More recently we have shown that the global electrophilicity index and its local counterpart may be used to characterize the reactivity pattern of the C=C double bond towards nucleophilic addition reactions. A wide family of molecules including ketones, esters, anhydrides, nitriles and nitrocompounds containing appropriate substitution on the C=C double bond have been classified within an unique scale of reactivity.[16] This index has been found to be almost insensitive to solvent effects for neutral electrophiles.[11] Thus, gas phase calculations suffice to establish the electrophilic power of molecules. Finally, we have shown that the intrinsic electronic contribution to the σ_p Hammett substituent constants, $\sigma_e(\omega)$, can be estimated from the ω index calculated for a series of substituted ethylenes.[12] EW substitution on ethylene increases the electrophilicity of molecules, and the corresponding $\sigma_e(\omega)$ values were consistently predicted as positive numbers.[12]

The aim of this paper is to show that despite the electron density accumulation observed in the ^{13}C NMR spectra,[4,5] the electrophilicity of these compounds does increase by substitution with EW groups.

2. Computational details

DFT calculations have been carried out using the B3LYP[17] exchange-correlation functionals, together with the standard 6-31G* basis set.[18] The optimizations were performed using the Berny analytical gradient optimization method.[19] The stationary points were characterized by frequency calculations in order to verify that minima and transition structures (TSs) have zero and one imaginary frequency, respectively. The intrinsic reaction coordinate (IRC)[20] path was traced in order to check the energy profiles connecting each TS to the two associated minima of the proposed mechanism, by using the second order González–Schlegel integration method.[21] The electronic structures of stationary points were analyzed by the natural bond orbital (NBO) method.[22] The solvent effects have been evaluated at B3LYP/6-31+G* level, as single point calculations performed on the gas-phase geometries. The method used was the self-consistent reaction field (SCRF)[23] based on the polarizable continuum model (PCM) of Tomasi's group.[24] All calculations were carried out with the Gaussian 98 suite of programs.[25]

3. Results and discussion

In order to evaluate the effects of EW substituents on the reactivity of the carbonyl compounds experimentally studied by Neuvonen et al.[4,5] the global electrophilicity of the substituted phenyl acetates **1a–f** and substituted phenyl dichloroacetates **2a–f** were studied (see Scheme 1). The ω indices for the whole series of molecules considered in this work together with the experimental rate coefficients for the alkaline hydrolysis of substituted phenyl acetates **1a–f**[26] and for the neutral hydrolysis of substituted phenyl dichloroacetates **2a–f**[4] are listed in Table 1. In Figure 1(a) we report a comparison between rate coefficients for the alkaline hydrolysis of substituted phenyl acetates **1a–f** and their corresponding global electrophilicity values. It may be seen that both quantities display a linear relationship ($R^2 = 0.98$) with a positive slope, thereby indicating that the increase in the reaction rates is correlated with an enhanced electrophilicity induced by EW substitution on the phenyl ring.
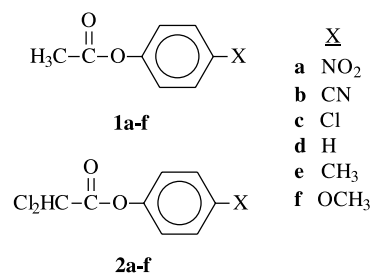
Scheme 1. Series of substituted phenyl acetates and phenyldichloro acetates.

In order to further test the quality of the regression equation (Eq. 2) to predict the experimental rate coefficients, we evaluated the electrophilicity index for the *p*-COMe, **1g**, and *p*-F, **1h**, phenyl derivatives not included in the Neuvonen's subseries **1a–f**. For **1g**, which has a $\omega = 1.64$ eV (see Table 1), the Eq. 2 predicts a value of $k = 17.30$ s^{-1} that is in a reasonably agreement with the experimental value of $k = 10.00$ s^{-1}.[26] For **1h**, which has a $\omega = 0.98$ eV (see Table 1),
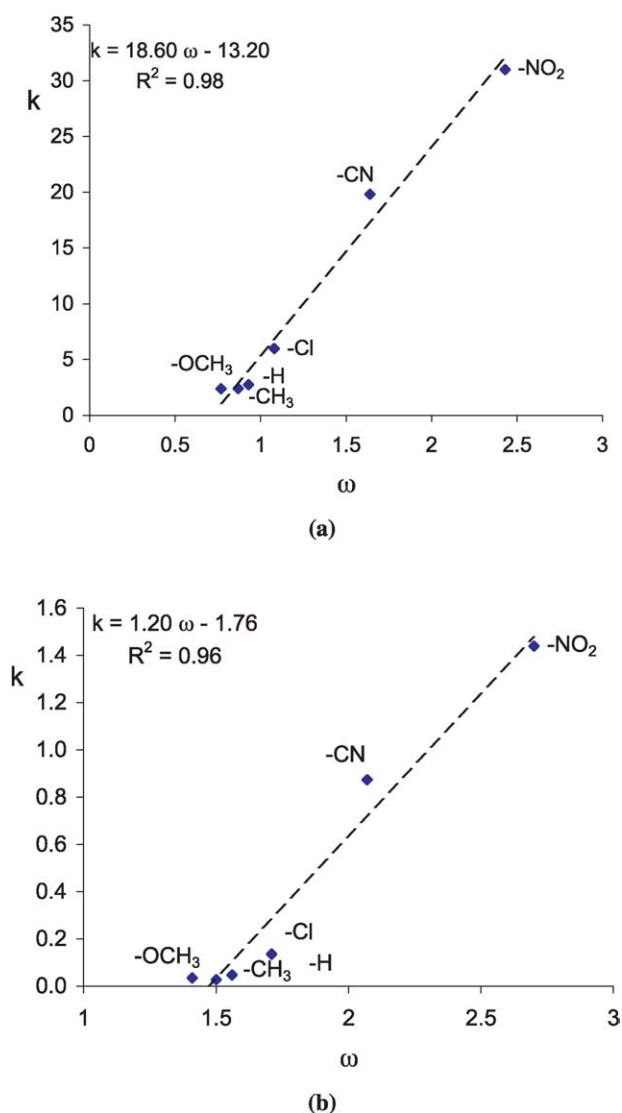
Figure 1. Comparison between rate coefficients and the electrophilicity index for (a) the alkaline hydrolysis of substituted phenyl acetates **1a–f** and (b) for the neutral hydrolysis of substituted phenyl dichloroacetates **2a–f**.

the predicted value of $k = 5.03 \text{ s}^{-1}$ is also in good agreement with the experimental value of $k = 4.20 \text{ s}^{-1}$.[26] Note that the predictive capability of Eq. 2 means in this context, that the estimated k values for the p-F and p-COMe derivatives are correctly lower and upper bounded by derivatives by weaker and stronger EW groups, respectively: phenyl acetate $<$ p-F-phenyl acetate $<$ p-Cl-phenyl acetate and p-Cl-phenyl acetate $<$ p-COMe-phenyl acetate $\approx$ p-CN-phenyl acetate (see Table 1). This result is useful if one consider that the variations in the rate coefficients fall within a narrow range. The second subseries **2a–f** is shown in Figure 1(b). In both cases the increase of the rate coefficients induced by increasing EW ability of the X substituent group is correlated with an enhanced electrophilicity.

$$k = 18.60 \, \omega - 13.20 \qquad (2)$$

Neuvonen et al.[4,5] proposed that the destabilization of the ground state (GS) induced by EW substitution could account for the increase of the reaction rate by means of a decrease in the activation energy: $\Delta E^{\neq} = E_{TS} - E_{GS}$. Isodesmic reactions were used to evaluate the GS destabilization for a series of X-substituted phenyl trifluoroacetates, phenyl dichloroacetates and phenyl acetates. In their study the energies were computed at the PM3 semiempirical level.

For the sake of simplicity, we evaluated the effects of the EW substitution on both GS stabilization and activation energy for the series of the X-substituted phenyl acetates **1a–f**. The GS destabilization energies were evaluated using the isodesmic model reaction shown in Scheme 2, and computing the total energies at the B3LYP/6-31G* level. The results are displayed in Table 2. An analysis of ΔE_{iso} values shows that substitution on the phenyl group destabilizes the GS relative to **1d** (X=H) by a small amount, ranging from 0.1 to 0.6 kcal/mol (see Table 2). In addition, substitution on the phenyl ring by π-electron-releasing groups, –Cl or –OMe, produces a larger destabilization of the GS than the π-electron-withdrawing ones, –NO$_2$ or –CN.

Table 1. Global properties[a] of the series for the substituents X for the substituted phenyl acetates **1a–f** and phenyl dichloroacetates **2a–f** and rate coefficients of the alkaline hydrolysis for the substituted phenyl acetates **1a–f**[b] and the neutral hydrolysis for the phenyl dichloroacetates **2a–f**[c]

	HOMO	LUMO	μ	η	ω	k
1a	−0.2698	−0.0892	−0.1795	0.1806	2.43	31.0
1b	−0.2576	−0.0547	−0.1561	0.2028	1.64	19.8
1c	−0.2407	−0.0225	−0.1316	0.2181	1.08	6.0
1d	−0.2402	−0.0105	−0.1254	0.2297	0.93	2.8
1e	−0.2308	−0.0082	−0.1195	0.2226	0.87	2.4
1f	−0.2139	−0.0036	−0.1087	0.2102	0.77	2.4
1g	−0.2479	−0.0562	−0.1521	0.1917	1.64	10.0
1h	−0.2381	−0.0149	−0.1265	0.2232	0.98	4.2
2a	−0.2824	−0.099	−0.1907	0.1833	2.70	1.440
2b	−0.2699	−0.0746	−0.1722	0.1953	2.07	0.874
2c	−0.2523	−0.0592	−0.1557	0.1932	1.71	0.136
2d	−0.2539	−0.0513	−0.1526	0.2026	1.56	0.048
2e	−0.2436	−0.0493	−0.1464	0.1943	1.50	0.027
2f	−0.2251	−0.0470	−0.1360	0.1781	1.41	0.035

[a] HOMO and LUMO energies, μ and η in a.u.; ω in eV.
[b] Rate coefficients (in s^{-1}) for the alkaline hydrolysis of compounds **1a–h** from Ref. 26.
[c] Rate coefficients (in s^{-1}) for the neutral hydrolysis of compounds **2a–f** from Ref. 4.
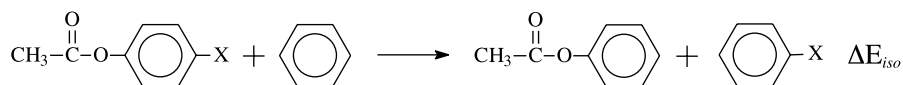
Scheme 2. Isodesmic model reaction used to evaluate the ground state destabilization energies ΔE_{iso} for substituted phenyl acetates **1a–f**.

Table 2. B3LYP/6-31G* total energies[a] (in a.u., including ZPE) and energies for the isodesmic reaction given in Scheme 2 (ΔE_{iso}, in kcal/mol)

	–X	X-Ph-OCOCH$_3$	Ph-X	ΔE_{iso}
1a	–NO$_2$	−664.481932	−436.647001	−0.13
1b	–CN	−552.227663	−324.392769	−0.16
1c	–Cl	−919.587983	−691.75375	−0.57
1e	–CH$_3$	−499.273428	−271.438396	−0.07
1f	–OCH$_3$	−574.471957	−346.637685	−0.55

[a] The total energies for benzene and methyl benzoate are −232.147878 and −459.983022 a.u., respectively.

The effects of the EW substitution on the activation energies were studied by computing the barriers for nucleophilic attack by the hydroxide ion on the subseries of substituted phenyl acetates **1a–f**. The gas-phase potential energy surfaces for these substitution reactions were explored by B3LYP/6-31G* calculations. One TS corresponding to a concerted process was found and characterized, in each case. The geometries of the TSs are given in Figure 2. An analysis of the geometries indicates that there is not an appreciable structural change induced by substitution on the phenyl acetate. The lengths of O–C forming bond, between 2.54–2.60 Å, and C–C breaking bonds, between 1.40–1.41 Å, indicate that these TSs correspond to early processes. Although the unique imaginary frequency characteristic of these TSs is associated to the atomic motion of the hydroxyl oxygen toward the carbonyl carbon,
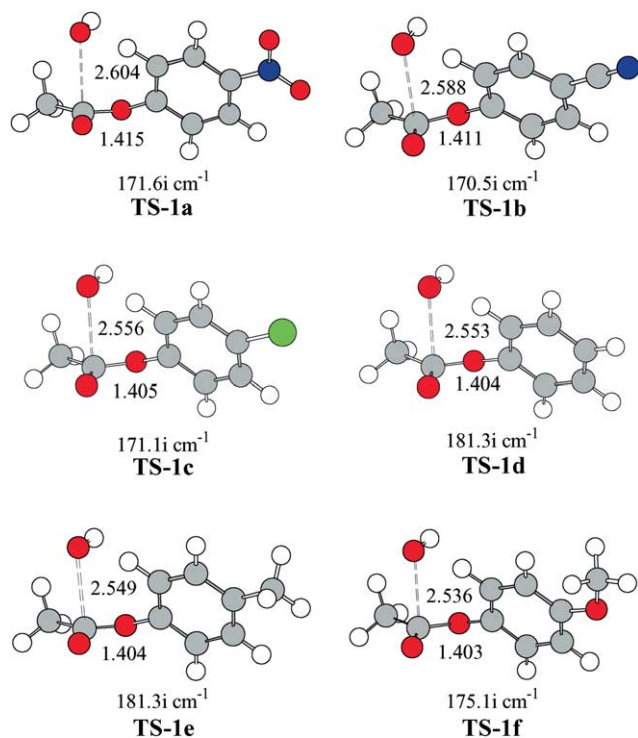
Figure 2. Transition structures corresponding to the nucleophilic attack of hydroxyl anion the substituted phenyl acetates **1a–f**. The bond lengths directly involved in the reaction are given in angstroms.

the IRC analysis from the TS to products asserts the concerted nature of these processes.

The barriers for nucleophilic attack of the hydroxyl anion to the whole subseries **1a–f** acetates were obtained at the B3LYP/6-31+G*(PCM)//B3LYP/6-31G* level. The predicted values of the activation energy, $\Delta E^{\neq}$, are comprised between 14.5 kcal/mol ($\omega = 2.43$ eV) and 17.2 kcal/mol ($\omega = 0.77$ eV) for the strong EW NO$_2$ and the electron releasing OCH$_3$ groups, respectively (see Table 2). This result stresses the linear relationship between increasing rate coefficient and enhanced electrophilicity of the substrate. The predicted barriers at this level of theory are reliable. For instance, for phenyl acetate **1d**, we obtain a value of $\Delta E^{\neq} = 16.1$ kcal/mol, which is in acceptable agreement with the experimental activation energy of 12.6 kcal/mol measured for hydrolysis in aqueous acetone. This result is also in agreement with previous work of Tantillo and Houk for the case of *p*-nitrophenyl acetate (**1a**).[27] The SCI-PCM solvation calculations predict a barrier for the concerted process associated with the *p*-nitrophenyl derivative **1a** 1.6 kcal/mol[27] lower than that for the reference phenyl acetate **1d** (a barrier lowering of 1.6 kcal/mol has been experimentally measured for this system[28]) (Table 3).

The energy analysis allows to draw up two main conclusions: (i) the GS destabilization with EW NO$_2$ substitution, 0.13 kcal/mol, is smaller than the reduction of the barrier, 1.64 kcal/mol, and as a result, the increase of the reaction rate is driven by a TS stabilization with the EW substitution, and (ii) the increase of the global electrophilicity by increasing the EW character of the substituent in the order H < Cl < CN < NO$_2$ causes a reduction of the barrier for the nucleophilic attack on the carbonyl group.

Table 3. B3LYP/6-31G* Total energies (E, in a.u., including ZPE) and B3LYP/6-31+G*(PCM)//B3LYP/6-31G* barriers ($\Delta E^{\neq} = (E_{TS} - E_{GS})$, in kcal/mol, including ZPE) in water for the nucleophilic attack of the hydroxyl anion on the phenyl acetates **1a–f**

	E	$\Delta E^{\neq}_{water}$
TS-1a	−740.2857732	14.50
TS-1b	−628.0293878	15.51
TS-1c	−995.3819359	17.49
TS-1d	−535.7679834	16.14
TS-1e	−575.0575821	16.07
TS-1f	−575.0522171	17.15

Scheme 3. Possible resonant structures for EW substituted phenyl acetates.

Note that this result is consistent with the global electrophilicity index evaluated for the whole series of phenyl esters **1a–f** and **2a–f** (see Fig. 1(a) and (b)).

For molecules of general type RC($=$O)Z:, the susceptibility to nucleophilic attack has been found to correlate with the reactivity of the acyl group, reflecting the resonance structures **I–III** in Scheme 3.[29] Neuvonen et al. proposed an increase of the π-electron density on the carbonyl carbon through a destabilization of structure **III**.[4,5] For phenyl-substituted esters an additional resonant structure **IV** can be draw which has only significance for EW groups. It provides double bond character of the carbonyl C–O bond, thereby allowing an additional explanation for the increase of the stretching frequencies in the IR spectrum. In addition, structure **IV** also provides an explanation for the upfield shift of the ^{13}C NMR chemical shift of the carbonyl carbon through a displacement of the π-electron density of the C–O double bond toward the carbonyl carbon.

4. Concluding remarks

In summary, the present study shows that the electrophilicity concept is better represented by the electrophilicity index proposed by Parr et al. than the population analysis-based quantities. The results obtained for the GSs of carbonyl compounds show that the electrophilicity increases with the EW substituent effects in these systems, and that inspite of the observed electron density accumulation at the carbonyl group, the enhanced electrophilicity induced by the EW groups in the substrates drives the nucleophilic attack at the carbonyl carbon. The analysis based on thermodynamic, ΔE_{iso}, and kinetic, $\Delta E^{\neq}$, energetic aspects shows that the effect of the EW substitution on the corresponding TS largely outweighs the energy destabilization in the GS. The present interpretation of the EW substitution effect on the carbonyl compounds is completely consistent with the kinetic data reported for these systems.

References and notes

1. Williams, A. *Concerted Organic and Bio-Organic Mechanism*; CRC: Boca Raton, 2000; Chapter 4 and references therein.
2. Kirby, A. J. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1980; p 161.
3. Connors, K. A. *Structure Reactivity Relationships: the Study of Reaction Rates in Solution*; VCH: New York, 1990; p 311.
4. Neuvonen, H.; Neuvonen, K. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1497.
5. Neuvonen, H.; Neuvonen, K.; Koch, A.; Kleinpeter, E.; Pasanen, P. *J. Org. Chem.* **2002**, *67*, 6995.
6. Murray, J. S.; Lane, P.; Brinck, T.; Politzer, P.; Sjoberg, P. *J. Phys. Chem.* **1991**, *95*, 844.
7. Pérez, P.; Toro-Labbé, A.; Aizman, A.; Contreras, R. *J. Org. Chem.* **2002**, *67*, 4747.
8. Pérez, P. *J. Phys. Chem. A* **2003**, *107*, 522.
9. Domingo, L. R.; Aurell, M. J.; Pérez, P.; Contreras, R. *Tetrahedron* **2002**, *58*, 4417.
10. Pérez, P.; Domingo, L. R.; Aurell, M. J.; Contreras, R. *Tetrahedron* **2003**, *59*, 3117.
11. Pérez, P.; Toro-Labbé, A.; Contreras, R. *J. Am. Chem. Soc.* **2001**, *123*, 5527.
12. Domingo, L. R.; Pérez, P.; Contreras, R. *J. Org. Chem.* **2003**, *68*, 6060.
13. Parr, R. G.; Szentpály, L. v.; Liu, S. *J. Am. Chem. Soc.* **1999**, *121*, 1922.
14. Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford Science: New York, 1994.
15. Mayr, H.; Kempf, B.; Ofial, A. R. *Acc. Chem. Res.* **2003**, *36*, 66.
16. Domingo, L. R.; Pérez, P.; Contreras, R. *Tetrahedron* **2004**, *60*, 6585.
17. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
18. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.
19. (a) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214. (b) Schlegel, H. B. Geometry Optimization on Potential Energy Surface. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1994.
20. Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161.
21. (a) González, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523. (b) González, C.; Schlegel, H. B. *J. Chem. Phys.* **1991**, *95*, 5853.
22. (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
23. (a) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027. (b) Simkin, B. Y.; Sheikhet, I. *Quantum Chemical and Statistical Theory of Solutions-A Computational Approach*; Ellis Horwood: London, 1995.
24. (a) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys.*

Lett. **1996**, *255*, 327. (b) Cances, M. T.; Mennunci, V.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032. (c) Barone, V.; Cossi, M.; Tomasi, J. *J. Comput. Chem.* **1998**, *19*, 404.

25. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; W. Gill, P. M.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.6, Gaussian, Inc.: Pittsburgh PA, 1998.

26. Nishioka, T.; Fujita, T.; Kitamura, K.; Nakajima, M. *J. Org. Chem.* **1975**, *40*, 2520.

27. Tantillo, D. J.; Houk, K. N. *J. Org. Chem.* **1999**, *6*, 3066. These authors recently studied the TSs for the addition-elimination reaction of phenyl acetate (**1d**) and hydroxide ion at the RHF/6-31+G* level. In the gas phase the reaction is concerted, but when aqueous solvation is considered through PCM and SCI-PCM calculations, the barrier to addition dramatically increases, and a stepwise addition-elimination pathway was predicted.

28. Tommila, E.; Hinshelwood, C. N. *J. Chem. Soc.* **1938**, 1801.

29. Sjoberg, P.; Politzer, P. *J. Phys. Chem.* **1990**, *94*, 3959.