Electronic Reduction of Haloaromatic Compounds. A Theoretical Study

Miquel Moreno, Iluminada Gallardo,* and Juan Bertrán
Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain

A series of haloaromatic molecules with a wide range of standard reduction potentials ($E°$) and bond-cleavage rate constants (k) has been studied using the MNDO semiempirical procedure. It has been found that the standard potential correlates better with the difference in energy between the radical anion and the neutral geometry when the geometry of the former is kept unchanged, in agreement with the Franck–Condon principle. A reaction co-ordinate study of the bond cleavage of the radical anion for the chloro derivatives shows the existence of two radical anions (π and σ) that differ in the orbital occupied by the unpaired electron. Whereas the π-radical anion is the most stable, the bond-breaking process takes place through the σ-structure. The study of the energies as well as of different molecular parameters related to the C–Cl bond cleavage allows us to explain qualitatively the experimental ordering of rate constants when different substituent groups are considered. However, the theoretical predictions do not account for the kinetic differences when only small structural changes are present. The significance of the solvent effect in these cases is pointed out.

Electrochemical methods as well as pulse-radiolysis have shown that the one-electron reduction of haloaromatic compounds in solution takes place through a radical anion that subsequently undergoes loss of the halogen,[1] as shown in the Scheme [reactions (1) and (2)].

$$\mathrm{ArX} + 1\mathrm{e} \longrightarrow \mathrm{ArX}^{-\bullet}\ (E°) \qquad (1)$$

$$\mathrm{ArX}^{-\bullet} \longrightarrow \mathrm{Ar}^{\bullet} + \mathrm{X}^{-}\ (k) \qquad (2)$$

Scheme.

In reaction (1), $E°$ is the standard reduction potential. For this reaction an important contribution to the free activation enthalpy comes from the solvent reorganization. However, given the size of the aromatic molecules there is only a relatively weak interaction with the solvent.[2]

The subsequent reaction of the haloaromatic radical anions [reaction (2)] takes place through cleavage of the carbon–halogen bond without any other noticeable change in the aromatic rings. The structural differences between the original molecules leads to a wide range of rate constant values k for the bond breaking of the radical anions.[3]

Quantum chemical calculations have been used in electrochemistry mainly to account for variations in the standard potential of the compounds with structure and Hammett-like relationships between reactivity and molecular structure.[4] Only recently has the advent of computers with increasing powers of calculation made feasible the attempt to correlate kinetic constants with quantum parameters[5] or to make predictions about reaction rates and find out a basis for the empirical rules.[6]

In the present work we will use quantum chemical models in order to characterize the electron-transfer reaction and the halogen–carbon bond cleavage. We will also try to correlate the theoretical parameters with the experimental results. Towards this aim we have chosen a series of nine haloaromatic compounds with a wide variation in $E°$ and k values. Table 1 shows the experimental parameters that have been previously reported by Saveant *et al.*[6a] The main goal of this work is to obtain a better understanding of the reactivity–structure relationships.

Table 1. Standard reduction potentials and bond-cleavage rate constants (log k) for the molecules studied.

Compound		$E°$/V *vs.* SCE[a]	log k[a]
(1)	Chlorobenzene	−2.78	>8
(2)	Bromobenzene	−2.44	>8
(3)	4-Chloroacetophenone	−1.90	5.5
(4)	3-Chloroacetophenone	−1.83	1
(5)	2-Chloroanthracene	−1.80	1.7
(6)	1-Chloroanthracene	−1.73	0.88
(7)	9-Chloroanthracene	−1.71	2.2
(8)	9-Bromoanthracene	−1.70	6.4–5.4
(9)	2-Chloronitrobenzene	−0.99	−2

[a] Ref. 6*a*.

Methodology.—All calculations were carried out using the semiempirical MNDO methodology of Dewar and Thiel.[7] The use of sophisticated high level *ab initio* calculations was prohibited because of the great size of the aromatic molecules considered in this study.

We have chosen the MNDO method among other semiempirical procedures because it has an elegant formalism and has been proved to be a most reliable technique.[8] However, a weakness of the method is its tendency towards an excessive stabilization of the π orbitals, particularly in aromatic systems.[9] This means that we are prevented from the use of absolute energy values to draw conclusions and so are constrained to an analysis of relative energies along a series of compounds with similar 'aromatic degree'.

RHF formalism has been used for closed-shell molecules whereas the UHF method is performed with open-shell structures.[10,11] UHF methodology is known to give satisfactory results when dealing with radical structures.[12]

The equilibrium geometries of all the molecules were fully optimized using the Davidon–Fletcher–Powell conjugated gradient algorithm.[13] The kinetics of the carbon–halogen bond-breaking in the radical anion is studied using the widespread reaction co-ordinate procedure. That is, taking the carbon–halogen distance as an independent variable we optimize, at a given set of points for the independent variable, the rest of the geometrical parameters. This finally leads to the energy profile of the reaction under consideration.

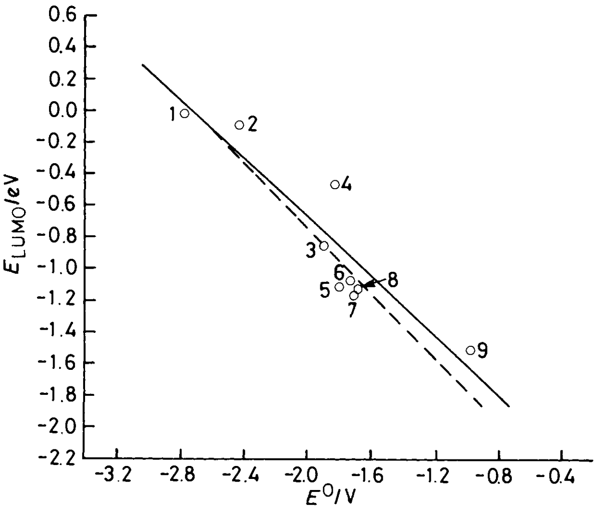

Figure 1. Correlation between the LUMO orbital energies and the standard reduction potentials in the haloaromatic series (same numbering as in Table 1). Slope: −0.942; correlation coefficient: 0.92; (——): obtained slope; (– – – –) slope, −1.

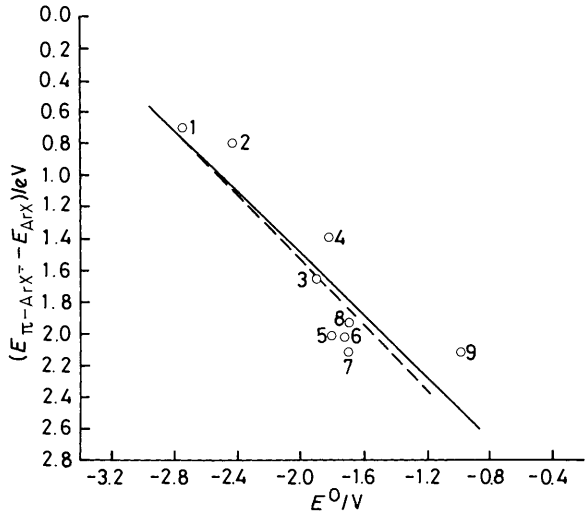

Figure 3. Correlation between the energetic differences of the radical anions at their optimized geometry with the neutral molecules and the standard reduction potentials in the haloaromatic series. Slope: −0.966; correlation coefficient: 0.87; (——): obtained slope; (– – – –) slope, −1.

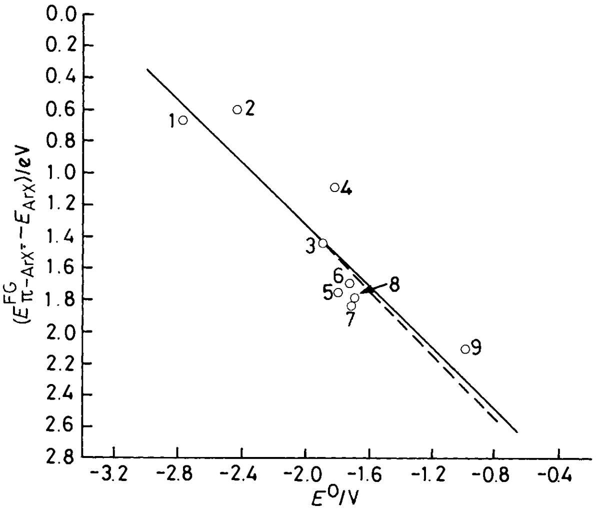

Figure 2. Correlation between the energetic differences of the radical anions at fixed geometry with the neutral molecules and the standard reduction potentials in the haloaromatic series. Slope: −0.976; correlation coefficient: 0.90; (——): obtained slope; (– – – –) slope, −1.

All the calculations were performed using the MOPAC[14] and AMPAC[15] programs.

Results and Discussion

We will start with a thermodynamic analysis of the neutral moleules and radical anions. Afterwards we will perform a kinetic analysis of the carbon–halogen bond cleavage. Finally, the possible role of other aspects of difficult computation such as the entropy and solvent effects in the comparison between theoretical and experimental results will be discussed.

Thermodynamic Study.—Classical relationships between E° and the LUMO energy of the neutral molecule have been settled. However, it has been shown thermodynamically that there is a linear correlation between electronic affinities and the standard reduction potential:[16]

$$FE^\circ = -(G^\circ_{\mathrm{ArX}^{\cdot-}} - G^\circ_{\mathrm{ArX}}) + G^\circ_{e})_{\mathrm{el}} - (\Delta G^\circ)_{\mathrm{SOLV}} \quad (1)$$

The first term on the right is the electronic affinity (if we do not take into account the entropic contribution).

So, it seems preferable to use the energetic differences between the radical anion and the neutral compound instead of the LUMO energy.

Two different geometries may be considered for the radical anion: the same geometry as the neutral molecule and the optimized geometry that comes from the minimization of the energy. According to the Franck–Condon principle[17] the moments and the positions of the nuclei do not change in the same time scale as the electronic transfer (10^{-14} s *vs.* 10^{-16} s). So the choice of a radical anion with the same geometry as the neutral molecule seems to be preferred in order to evaluate the electronic affinity.

Figures 1–3 depict, respectively, (*versus* E°/V): (*a*) the energy of the LUMO orbital for the neutral molecule (E_{LUMO}) and (*b*) the energetic differences between the radical anion at fixed and optimized geometry and the neutral molecule ($E^{\mathrm{FG}}_{\pi\text{-}\mathrm{ArX}^{\cdot-}} - E_{\mathrm{ArX}}$ and $E_{\pi\text{-}\mathrm{ArX}^{\cdot-}} - E_{\mathrm{ArX}}$) (in eV).

In agreement with equation (1) (neglecting the entropic effects and considering the solvent contribution to be approximately constant for the compounds studied) the slopes of the analysed correlations should be *ca.* −1. Effectively, the slopes obtained using the least-squares procedure have the values −0.94, −0.98, and −0.97, respectively. The first (E_{LUMO} *vs.* E°) is the case classically considered and it already points out the expected dependency. Nevertheless, the two correlations with energetic differences show a better approximation to the theoretical value.

The similarity between the last two slopes (0.98 and −0.97) would be expected if we considered that there were only slight geometrical differences between the neutral species and the radical anion. However, the correlation coefficients for these two cases (0.90 and 0.87) give a better correlation when using the fixed-geometry radical anions. This agrees with the Franck–Condon principle.[17]

The obtained results seem, therefore, to point out a better dependency of the standard reduction potentials E° on the electronic transfer without intervention of the posterior geometric changes in the radical anion.

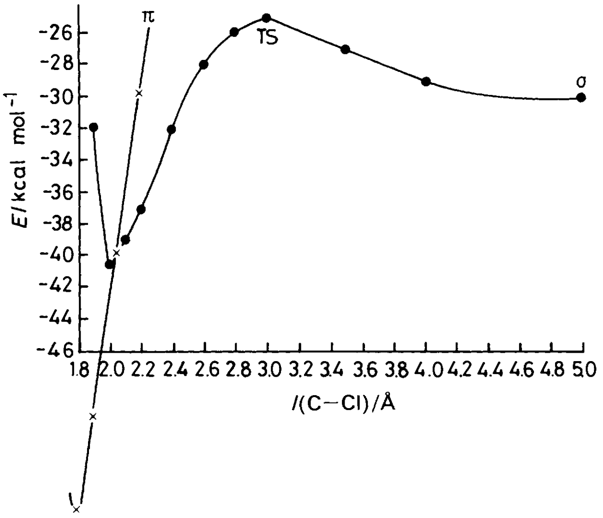

Figure 4. Energy profiles for the σ- and π-radical anions of 3-chloronitrobenzene (**9**) along the C–Cl bond.

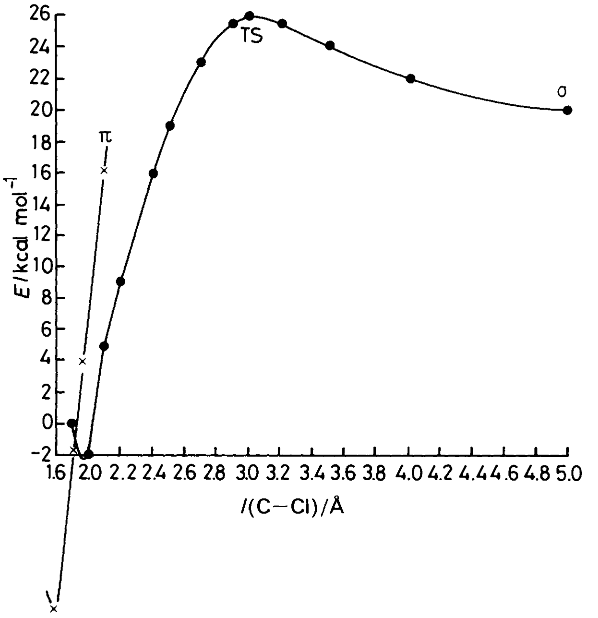

Figure 5. Energy profiles for the σ- and π-radical anions of 3-chloroacetophenone (**4**) along the C–Cl bond.

Kinetic Study.—Of the different techniques developed to study theoretically the kinetics of a chemical process we have used the well-known reaction co-ordinate method, given that in this kind of reaction there is clearly only one geometrical parameter (bond distance carbon–halogen l_{C-X}) the variation of which represents the degree of progress of the bond-cleavage reaction.

Given the size of the molecules studied we are confined to the substituted halobenzenes in this study. In particular, we chose the chloro derivatives in order to have a wider comparative range. Later on, and consistently with the obtained results, we will take into consideration the possibility of extending this analysis to the anthracenes.

Figures 4 and 5 depict the energetic profiles of the bond cleavage for the radical anions corresponding to compounds (**4**) and (**9**), respectively. In these Figures we can see that an increase in the bond distance C–Cl of the π-radical anions (the π-prefix is used here to indicate that the additional electron lies in a π-type orbital) gives rise to a quick increase in energy so that the radical anion becomes unstable. However, at these points a more stable electronic structure with the unpaired electron located in a σ-orbital has been found. This σ-orbital is, basically, antibonding between the halogen and the adjacent carbon atom. If we follow the bond breaking process through this σ-radical anion we obtain the stable final product of the reaction: the aromatic radical (Ar$^{\bullet}$) plus the chloride anion (Cl^{-}), in accordance with the experimental evidence.

The crossing point between both energetic profiles designates the $\pi \longrightarrow \sigma$ electronic transition. This point matches the energetic minimum of the σ-radical anion ($E_{\sigma\text{-ArCl}^{-\bullet}}$) with an error margin of ± 0.1 Å in the reaction co-ordinate value. The same result was previously reported in a similar study on chlorobenzene.[6b]

Further useful information that can be extracted from an analysis of the energetic profiles comes from the position and energy of the transition state for the σ-bond breaking (points marked TS in Figures 4 and 5). In both cases we notice that the C–Cl distance is great so that the bond is almost broken and the transition state is geometrically close to the final products. Again this result agrees with the previous work on chlorobenzene.[6b]

We conclude therefore that it is a good approximation to consider the energies and structures of the energetic minimum of the radical anion and the final product (Ar$^{\bullet}$ + Cl^{-}) instead of the $\pi \longrightarrow \sigma$ crossing point and the transition state respectively. The energies of the former points are shown in Table 2 for all the aromatic chloro derivatives considered to date.

According to the literature[18] one would expect, from the results in Table 2, to find a good correlation between the rate constant (log k) and the $\pi \longrightarrow \sigma$ electronic transfer ($E_{\sigma\text{-ArCl}^{-\bullet}} - E_{\pi\text{-ArCl}^{-\bullet}}$). However, our quantum chemical calculations do not support this relationship.

On the contrary, the results show a good interrelation between the experimental reactivity and the cleavage of the σ-radical anion ($E_{\text{Ar}^{\bullet}+\text{Cl}^{-}} - E_{\sigma\text{-ArCl}^{-\bullet}}$). So, our results predict that the rate-determining step for the bond-cleavage reaction is the σ-radical anion bond-breaking instead of the $\pi \longrightarrow \sigma$ electronic transition, even when the energetic barrier for the latter is higher. We must remember the excessive stabilization of the π-structure due to methodological errors already cited.[9] Anyway, we note that with the exception of *o*-chloronitrobenzene (**9**), the energetic differences are not split sufficiently in order to draw definite conclusions. So in order to have a deeper insight into the results, it would seem interesting to account for different molecular properties.

In Table 3 the parameters we expect to be more directly related to the cleavage of the C–Cl bond are displayed for the π- and σ-radical anions and the neutral molecule: the bond order C–Cl, the total charge in the chlorine atom, and the C–Cl bond length.

As a general trend we observe that the bond order is almost equal in the neutral molecule and the π-radical anion but it has dramatically decreased in the σ-radical anion. At the same time we note in the σ-radical anion an important increase in the negative charge in the chlorine atom and of the C–Cl bond length. As before with the energy analysis (Table 2) the differences between compounds are not significant. Only the 2-chloronitrobenzene (**9**) shows deviant behaviour, its σ-radical anion having a much less broken C–Cl bond than the other three.

A study analogous to that reported for the benzenes has been carried out for the three chloroanthracenes. Table 4 shows the energetics as well as the bond orders, charges, and distances for the C–Cl bond. The observed differences between the three

Table 2. Energy differences between the σ- and π-radical anions ($E_{\sigma\text{-ArCl}^{\cdot-}} - E_{\pi\text{-ArCl}^{\cdot-}}$) and between the products of the reaction and the σ-radical anions ($E_{\text{Ar}^{\cdot}+\text{Cl}^{-}} - E_{\sigma\text{-ArCl}^{\cdot-}}$) for the indicated substituted benzenes.

Compound[a]	log *k*	$(E_{\sigma\text{-ArCl}^{\cdot-}} - E_{\pi\text{-ArCl}^{\cdot-}})^b$	$(E_{\text{Ar}^{\cdot}+\text{Cl}^{-}} - E_{\sigma\text{-ArCl}^{\cdot-}})^b$
(1)	>8	6.2	12.8
(3)	5.5	20.5	13.1
(4)	1.0	15.6	16.7
(9)	−2.0	8.8	27.2

[a] Same numbering as in Table 1. [b] kcal mol^{-1}.

Table 3. Quantum chemical properties of the neutral molecule and the π- and σ-radical anions for the indicated compounds.

Compound[a]		**(1)**	**(3)**	**(4)**	**(9)**
Bond order C–Cl	Ar–Cl	0.96	0.97	0.97	0.99
	π-Ar–Cl	0.95	0.91	0.90	0.92
	σ-Ar–Cl	0.24	0.26	0.28	0.79
q_{Cl}/a.u	Ar–Cl	−0.11	−0.10	−0.10	−0.05
	π-Ar–Cl	−0.26	−0.22	−0.23	−0.19
	σ-Ar–Cl	−0.63	−0.60	−0.60	−0.34
$l_{\text{C–Cl}}$/Å	Ar–Cl	1.75	1.75	1.75	1.75
	π-Ar–Cl	1.78	1.77	1.78	1.78
	σ-Ar–Cl	2.00	1.98	2.00	2.00

[a] Same numbering as in Table 1.

Table 4. Energies and quantum chemical properties for the three isomers of chloroanthracene.

Compound[a]		**(5)**	**(6)**	**(7)**
log *k*		1.7	0.88	2.2
$(E_{\sigma\text{-ArCl}^{\cdot-}} - E_{\pi\text{-ArCl}^{\cdot-}})$/kcal mol^{-1}		17.2	15.9	15.6
$(E_{\text{Ar}^{\cdot}+\text{Cl}^{-}} - E_{\sigma\text{-ArCl}^{\cdot-}})$/kcal mol^{-1}		28.6	27.7	27.4
Bond order C–Cl	Ar–Cl	0.97	0.96	0.96
	π-Ar–Cl	0.91	0.92	0.90
	σ-Ar–Cl	0.25	0.25	0.24
q_{Cl}/au	Ar–Cl	−0.11	−0.11	−0.11
	π-Ar–Cl	−0.21	−0.20	−0.20
	σ-Ar–Cl	−0.61	−0.62	−0.62
$l_{\text{C–Cl}}$/Å	Ar–Cl	1.75	1.75	1.76
	π-Ar–Cl	1.76	1.77	1.76
	σ-Ar–Cl	1.97	1.99	2.00

[a] Same numbering as in Table 1.

Table 5. Dipolar moments (D) for the neutral chloroanthracenes compared with the kinetic constants.

Compound[a]	log *k*	μ
(5)	1.7	1.68
(6)	0.88	2.12
(7)	2.2	1.64

[a] Same numbering as in Table 1.

isomers are within the range of the methodological errors so that our results cannot account for the different kinetic behavior experimentally observed.

Therefore, the obtained quantum mechanical results qualitatively explain the experimental behaviour of compounds with different substituents. However, the calculations fail to show significative differences when there are only small structural changes such as for the three isomers of chloroanthracene. On the other hand our results point out that the cleavage of the C–Cl bond in the σ-radical anion is the rate-determining step for the considered reaction.

Entropy and Solvent Effects.—Given the fact that the previous results do not account for the observed kinetic differences between the structural isomers of chloroanthracene, one could believe that the evaluation of the entropic term is important. Up to now we have considered this term to be negligible or, at least, constant for a given family of molecules. In order to test this view we have evaluated theoretically the entropy for the chloroanthracenes.

Calculations have been carried out by numerical computation and diagonalization of the Hessian matrix and by using the statistical thermodynamic formulae within the ideal gas, rigid rotor, and harmonic oscillator models.[19]

For the neutral molecules **(5)**–**(7)** we have obtained, at a pressure of 1 atm and a temperature of 298.15 K, the values 89.9, 87.7, and 86.3 cal mol^{-1} K^{-1}, respectively.* We have not been able to evaluate the entropy for the radical anions because the computations were too long. It is observed, however, that the span in TS values is small (*ca.* 1 kcal mol^{-1}) between the three cases considered so it is expected that the introduction of the entropy term will not noticeably change the results obtained. The computation of the entropy term for the whole series of radicals studied here is beyond our present computational capabilities.

Another factor we may have to consider is the solvent effect. This arises from the fact that experimental results have been obtained in solution whereas the quantum mechanical calculations refer to the isolated molecules, that is, in the gas phase. As we have not been able to perform a rigorous study using a discrete or continuous model for the solvent, we will use the dipole moment of the neutral molecule as an indication of the relative importance of the solvent effect.

We must stress the fact that the main solvent effect comes from the negatively charged species.[20] However, in the products the charge is always in the same compound (chloride), the dipolar moment of the radicals being similar and small (0.4–0.7 D). In the radical anions we have already noted the very small electronic differences between compounds so we may suppose that the kinetic distinction between them still comes from the dipole moments. Finally we must also assume that the ordering of dipole moments for the neutral molecules is kept unchanged in the radical anions.

The values of dipole moment compared with rate constant are presented in Table 5 for the three chloroanthracenes. We see a good correlation between increasing dipole moment and decreasing rate constant. That is, if the molecule has a larger solvation free enthalpy the rate constant is, consequently, smaller. This study seems to suggest that further work devoted to a more systematic and quantitative study of the solvent effect for this kind of reaction is required.

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* 1 cal = 4.184 J.

Conclusions

The standard reduction potential (E°) is related to the electron transfer which takes place with no geometrical change in the radical anion. We suggest that the rate-determining step of the bond-cleavage reaction is the breaking of the C–Cl bond in the σ-radical anion. We have shown the necessity of invoking the solvent effect in order to explain the kinetic differences which are experimentally observed when dealing with only small structural changes in the solute.

References

1 (*a*) M. D. Hawley in 'Encyclopedia of Electrochemistry of the Elements,' eds. A. J. Bard and H. Lund, Marcel Dekker, New York, 1980, vol XIV, Organic section; (*b*) J. Y. Becker in 'The Chemistry of Functional Groups,' Suppl. D, eds. S. Patai and Z. Rappoport, Wiley, New York, 1983, ch. 6; (*c*) R. K. Norris, S. D. Barker, and P. Neta, *J. Am. Chem. Soc.*, 1984, **106**, 3140, and references cited therein.

2 A. J. Bard and H. Kojima, *J. Am. Chem. Soc.*, 1975, **97**, 6317, and references cited therein.

3 (*a*) C. P. Andrieux, C. Blocman, J. M. Dumas-Bouchiat, F. M'Halla, and J. M. Saveant, *J. Am. Chem. Soc.*, 1980, **102**, 3806; (*b*) M. Falsig, H. Lund, L. Nadjo, and J. M. Saveant, *Nouv. J. Chim.*, 1980, **4**, 445.

4 (*a*) A. Streitwieser in 'Molecular Orbital Theory for Organic Chemists,' J. Wiley and Sons, New York, 1961, 1967, ch. 7; (*b*) M. J. S. Dewar and R. C. Dougherty in 'The PMO Theory of Organic Chemistry,' Plenum Press, New York, 1975, ch. 7.

5 J. M. Hale in 'Reactions of Molecules at Electrodes,' N. S. Hush, ed., Wiley-Interscience, New York, 1971, ch. 4.

6 (*a*) C. P. Andrieux, J. M. Saveant, and D. Zann, *Nouv. J. Chim.*, 1984, **2**, 107, and references cited therein; (*b*) J. Casado, I. Gallardo, and M. Moreno, *J. Electroanal. Chem. Interfacial*, 1987, **219**, 197.

7 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899 and 4907.

8 See *e.g.* T. Clark in 'A Handbook of Computational Chemistry,' J. Wiley and Sons, New York, 1985, p. 148 and references cited in p. 192.

9 M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, 1978, **100**, 784.

10 C. C. J. Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.

11 J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, 1974, **22**, 571.

12 (*a*) R. J. Duchovic, W. L. Hase, and H. B. Schlegel, *J. Phys. Chem.*, 1984, **88**, 1339; (*b*) M. N. Paddon-Row and J. A. Pople, *ibid.*, 1985, **89**, 2768; (*c*) K. N. Houk, M. N. Paddon-Row, D. C. Spellmeyer, N. G. Rondan, and S. Nagase, *J. Org. Chem.*, 1986, **51**, 2874.

13 R. Fletcher and M. D. Powell, *Comput. J.*, 1963, **6**, 163; W. C. Davidon, *ibid.*, 1968, **10**, 406.

14 J. J. P. Stewart, *QCPE Bull.*, 1986, **6**, 91; *QCPE*, program 455, version 3.1.

15 M. J. S. Dewar and J. J. P. Stewart, *QCPE Bull.*, 1986, **6**, 24; *QCPE* program 506.

16 M. J. S. Dewar, J. A. Hashmall, and N. Trinajstic, *J. Am. Chem. Soc.*, 1970, **92**, 5555.

17 F. L. Pillar in 'Elementary Quantum Chemistry,' McGraw–Hill, New York, 1968, ch. 15.

18 J. P. Bays, S. T. Blumer, S. Baral–Tosh, D. Behar, and P. Neta, *J. Am. Chem. Soc.*, 1983, **105**, 320.

19 D. McQuarrie in 'Statistical Mechanics,' Harper and Row, New York, 1976, ch. 8.

20 J. G. Kirkwood, *J. Chem. Phys.*, 1934, **2**, 4351.

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