The Stabilization of α-Substituted Oxy- and Thiocarbanions

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Abstract: In this paper we report the results obtained in an ab initio study at an extended level of the effects of the oxy and thio substituents upon the stabilities of α-substituted carbanions. To rationalize this problem, we have decomposed the stabilization energies into the component terms associated with the σ effects, the nonbonded interaction effects, the 3d orbitals effects, and the correlation energy effects. At all levels of computations used in this investigation it is found that the SH group stabilizes the anionic center more than the OH group and that this trend is determined by the σ effects. The present analysis has shown also that the effect of the nonbonded interaction favors OH over SH and that the contribution of the sulfur 3d orbitals is very small. More significant appears to be the contribution associated with the correlation energy effects, which favors SH over OH.

1. Introduction

Carbanions are very reactive species and play an important role in the chemical syntheses[1] as well as in physical organic chemistry.[2] One of the most important groups of carbanions is represented by carbanions of the type $R_2\bar{C}$–X formed in an α position to a heteroatom X. In these species it is known experimentally that second-row heteroatoms such as sulfur and chlorine stabilize the adjacent anionic center more than the corresponding first-row heteroatoms oxygen and fluorine.[3]

Various types of effects have been proposed to explain these trends.[4-12] These include effects associated with various types of nonbonded interactions (d orbital conjugation, lone pair–lone pair repulsions, hyperconjugative interactions), polarization effects, and σ effects. However, the relative importance of these effects has never been estimated quantitatively. In this paper we report the results obtained in an ab initio SCF-MO study at an extended level, where we have analyzed the factors that influence the stabilization of a carbanionic center by adjacent OH and SH groups. The systems chosen for the discussion are the Y and W conformations of the two carbanions $H_2\bar{C}$–OH and $H_2\bar{C}$–SH (see Scheme I); these conformations are energy minima on the rotation–inversion surface of both carbanions.[4,7]

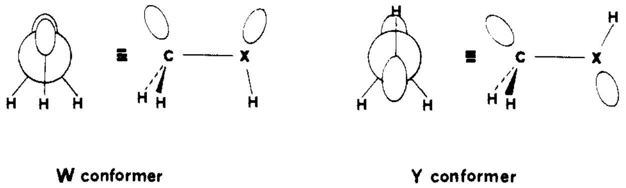
2. Computational Results

In all cases we have computed accurate stabilization energies. Then we have decomposed the stabilization energies into the component terms associated with the various types of effects that can be assumed to play a certain role in the stabilization process. These are the following: (i) σ effects, (ii) nonbonded interaction effects, (iii) d orbital effects, and (iv) correlation energy effects. All the component terms associated with the various types of effects have been computed in terms of SCF-MO total energy values. The contributions associated with the σ and the nonbonded interaction effects have been computed by using total energy values obtained in the absence of the interaction under examination (total energy approach),[13a,b] while those associated with the d orbital and correlation energy effects have been determined by using total energy values obtained with and without the d orbitals in the basis set or the correlation energy corrections. Detailed informations about the energy effects associated with the various orbital interactions have also been obtained by using a quantitative PMO analysis.[13]

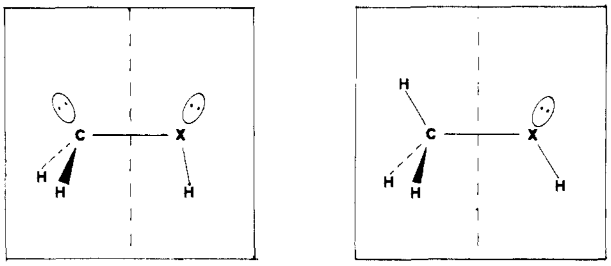
The stabilization energies (SE) associated with the two substituents OH and SH have been computed on the basis of the following equation[14]

$$SE = [E_T(H_3C{-}XH) + E_T(CH_3^-)] - [E_T(H_2\bar{C}{-}XH) + E_T(CH_4)] \qquad (1)$$

Scheme I



Scheme II



where E_T represents the SCF-MO total energy value. Positive values of SE mean that a given substituent stabilizes the anionic

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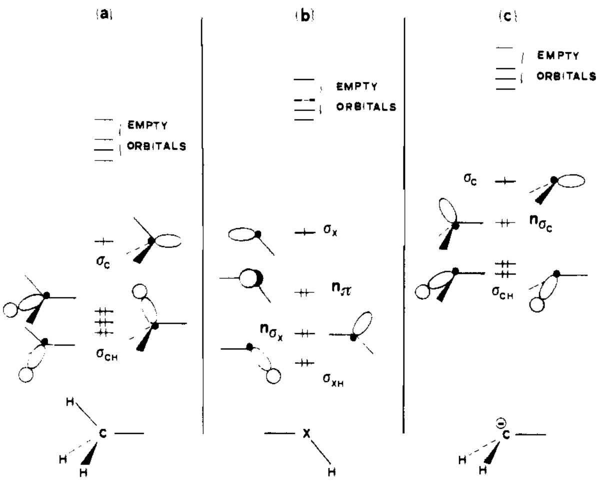


Figure 1. Fragment localized MO's obtained for (a) the H_3C- fragment, (b) the $-XH$ fragment with X = O, S, and (c) the $H_2\bar{C}-$ fragment.

center more than H, while negative values mean the reverse.

For each molecular system we have used fully optimized geometries, obtained with analytical gradient procedure.[15] In particular for the neutral molecules we have used the 3-21G[16a] optimized geometries, while for the carbanions the 3-21+G[17] (i.e., 3-21G augmented with a set of diffuse functions) optimized geometries. For the sulfur derivatives we have also used the geometries optimized with the corresponding basis sets augmented with the sulfur 3d orbitals, i.e., the 3-21G*[16b] optimized geometry for H_3C-SH and the 3-21+G*[17] optimized geometry for $H_2\bar{C}-SH$. All these geometries have already been reported (see ref 18).

In order to obtain more accurate energy values to be used in the comparative analysis of the effect of the two substituents OH and SH, we have performed single-point computations on the 3-21G and 3-21+G optimized geometries at the 6-31+G[17] level where we have inserted diffuse p functions on the carbanion center only. Similar single-point computations have also been performed with the 6-31+G* basis set[17] on the 3-21G* and 3-21+G* optimized geometries of H_3C-SH and $H_2\bar{C}-SH$. Finally single-point computations at the MP2/6-31+G* level (i.e., with second-order Møller-Plesset correlation energy corrections[19]) have been carried out on the 3-21G and 3-21+G optimized geometries of H_3C-OH and $H_2\bar{C}-OH$ and on the 3-21G* and 31-21+G* optimized geometries of H_3C-SH and $H_2\bar{C}-SH$, respectively.

The total energy values in the absence of the nonbonded interactions as well as the PMO estimates of the energy effects associated with these interactions have been computed with the procedures described in ref 13. In these computations we have used a basis of fragment localized orbitals (computed with the methods described in ref 13) with the various molecules dissected as shown in Scheme II. The resulting fragment localized orbitals are shown in Figure 1.

Table I. Stabilization Energies SE (Kcal/mol) of the α-Substituted Oxy- and Thio carbanions Computed at the 6-31+G, 6-31+G*, and MP2/6-31+G* Levels

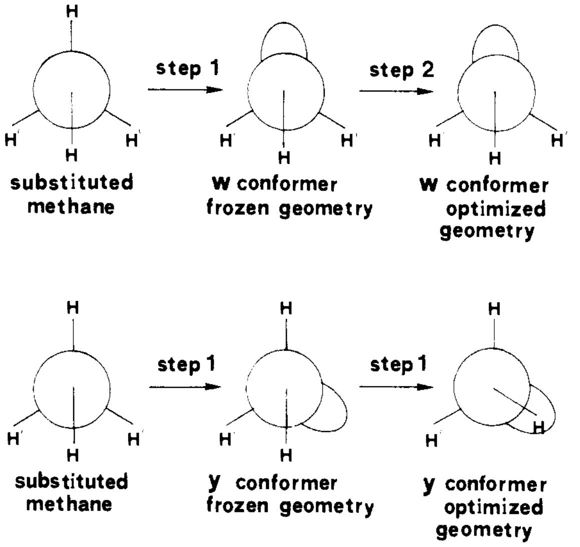
	$H_2\bar{C}-X$		
X	6-31+G// 3-21+G	6-31+G*// 3-21+G	MP2/6-31+G*// 3-21+G*
		W Conformer	
OH	−2.23		0.24
SH	18.81	18.63	27.95
		Y Conformer	
OH	3.76		5.30
SH	19.75	17.43	26.74

Table II. Total Energies (au) of Substituted Methanes (H_3C-X) and Related Carbanions ($H_2\bar{C}-X$) Computed with (E_T) and without ($E_T°$) Nonbonded Interactions

		6-31+G//3-21+G		6-31+G*//3-21+G*	
		E_T	$E_T°$	E_T	$E_T°$
H_3C-OH		−114.98964	−115.27847		
H_3C-SH		−437.64810	−437.83626	−437.68287	−437.93578
	W[a]	−114.29190	−114.64680		
$H_2\bar{C}-OH$	W[b]	−114.29533	−114.52864		
	Y[a]	−114.29213	−114.65133		
$H_2\bar{C}-OH$	Y[b]	−114.30488	−114.54048		
	W[a]	−436.98232	−437.27518	−437.01626	−437.35153
$H_2\bar{C}-SH$	W[b]	−436.98732	−437.19649	−437.02181	−437.33167
	Y[a]	−436.97673	−437.24338	−437.00729	−437.32718
$H_2\bar{C}-SH$	Y[b]	−436.98882	−437.14200	−437.01989	−437.30425

[a] Geometry of the related substituted methane (frozen geometry, see Scheme IV). [b] Optimized geometry.

Scheme III



The results reported in this paper have been obtained by using the GAUSSIAN 80 series of programs,[20] implemented also with some additional computer codes to perform the quantitative PMO analysis and to evaluate the total energy $E_T°$ in the absence of nonbonded interactions.

3. Results and Discussions

The stabilization energy values SE computed at the various levels are summarized in Table I. The analysis of these results shows that at all levels of computation investigated here the SH group stabilizes the anionic center more than the OH group, and

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Table III. OH and SH Stabilization Energies (SE) Computed at the 6-31+G and 6-31+G* Levels and Related Contributions Associated with the σ (SE(σ)) and the Nonbonded Interactions (SE(NB)) Effects

	X = OH		X = SH[a]		X = SH[b]	
	frozen	optimized	frozen	optimized	frozen	optimized
			W Conformer			
(C–X)	1.440	1.557	1.894	2.017	1.825	1.769
SE	-4.39	-2.23	15.67	18.81	15.15	18.63
SE(σ)	37.07	-37.07	81.37	31.99	66.81	54.37
SE(NB)	-41.46	34.83	-65.70	-13.18	-51.66	-35.72
			Y Conformer			
(C–X)	1.440	1.559	1.894	2.058	1.825	1.804
SE	-4.24	3.76	12.16	19.75	9.52	17.43
SE(σ)	39.92	-29.64	61.41	-2.20	51.53	37.15
SE(NB)	-44.16	33.40	-49.26	21.95	-42.01	-19.72

[a] Without d-orbitals on Sulfur (6-31+G). [b] With d-orbitals on sulfur (6-31+G*).

the inclusion of the sulfur 3d orbitals and of the energy correlation contributions has only minor effects.

In order to understand the energy effects involved in the formation of a carbanion, we have decomposed the formation process in the following two steps (see Scheme III): (a) step 1, where we remove a proton from the methyl group of the methyl derivative, obtaining a carbanion with the geometry of the related substituted methane (frozen carbanion); (b) step 2, where we relax the geometry, obtaining the carbanion in its optimized geometry (optimized carbanion).

For each step we have computed the following: (i) the E_T values and related stabilization energies SE; (ii) the $E_T°$ values and related stabilization energies SE(σ) (see the following discussion); (iii) the $E_T - E_T°$ values.

With the second-row substituent, these computations have been performed without and with sulfur 3d orbitals. The E_T and $E_T°$ values are listed in Table II.

These computations allow us to decompose the SE values in two components

$$\mathrm{SE} = \mathrm{SE}(\sigma) + \mathrm{SE(NB)} \qquad (2)$$

where SE(σ) is the contribution associated with the effects of the C–X bond (σ effects) and is computed in terms of the $E_T°$ values according to eq 1, while SE(NB) is the contribution associated with the effects of the nonbonded interactions and is computed according to the following expression

$$\mathrm{SE(NB)} = (E_T - E_T°)_{\mathrm{H_3CX}} - (E_T - E_T°)_{\mathrm{H_2\bar{C}X}} \qquad (3)$$

where $(E_T - E_T°)_{\mathrm{H_3CX}}$ and $(E_T - E_T°)_{\mathrm{H_2\bar{C}X}}$ denote the energy effects associated with the nonbonded interaction in the substituted methane and related carbanion, respectively. The SE(σ) and SE(NB) values computed for the "frozen" and "optimized" carbanions at the 6-31+G and 61-31+G* levels are listed in Table III, while the ($E_T - E_T°$) values are listed in Table IV. The analysis of the SE values listed in Table III shows that the trend that the SH group stabilizes the anionic center more than the OH group is found not only at the level of the "optimized" carbanions but already at the level of the "frozen" carbanions. Furthermore, for both oxy- and thiocarbanions the stabilization energy SE is not significantly modified with the relaxation of the carbanion geometry, the variations being more pronounced in the Y than in the W conformer.

We attempt now to understand in detail the role of the various factors.

We consider first the results obtained at the 6-31+G level, i.e., without 3d orbitals on sulfur. The comparative analysis of the values of Table III shows that at the level of the "frozen carbanion" the SE(NB) contribution is destabilizing and favors OH over SH, while the SE(σ) contribution is stabilizing and favors SH over OH. The latter contribution dominates, and, therefore, at this level the thiocarbanion is more stabilized because of a larger σ effect.

The negative sign of the SE(NB) contribution indicates that the removal of a proton in these species is accompanied by an increase of the repulsive effects associated with the nonbonded interactions. To reduce these large destabilizing effects the geometry tends to change and in both types of carbanions the main variation is associated with a significant lengthening of the C–X bond length, as shown by the r(C–X) values listed in Table III. However, the lengthening of the C–X bond is also accompanied by a decrease of the stabilization of the C–X bond in the carbanions. The two effects, decrease of the nonbonded repulsions and decrease of the stabilization of the C–X bond, are of similar order of magnitude, so that the overall stabilization energy remains almost unchanged with the relaxation of the carbanion geometry. Therefore at the optimized geometry it is again SE(σ) that determines the trend of the stabilization energy, and, consequently, the thiocarbanion is more stabilized than the oxycarbanion because of the σ-effect.

Table IV. Energy Effects[a]: (kcal/mol) Associated with the Nonbonded Interactions in the $H_3C–XH$ and Related $H_2\bar{C}–XH$ Species (XH = OH, SH)

		W($H_2\bar{C}$–XH)		Y($H_2\bar{C}$–XH)	
	H_3C–XH	frozen	optimized	frozen	optimized
		XH = OH			
$E_T - E_T°$	181.24	222.70	146.10	225.40	147.84
$\Sigma\Delta E^4$	42.65	65.36	49.89	73.28	52.12
$\Sigma\Delta E^2$	-12.89	-18.52	-18.71	-14.57	-14.93
		XH = SH			
$E_T - E_T°$	118.07	183.77	131.25	167.33	96.12
$\Sigma\Delta E^4$	34.97	52.09	40.49	55.90	38.12
$\Sigma\Delta E^2$	-7.08	-11.63	-12.79	-8.05	-11.10
$\Sigma\Delta E_{3d}{}^2$	-4.36	-6.82	-7.33	-6.80	-7.10

[a] The $E_T - E_T°$, ΔE^4 and ΔE^2 values have been computed at the 6-31+G level, while $\Delta E_{3d}{}^2$ at the 6-31+G* level.

The inclusion of the 3d orbitals of sulfur modifies significantly the geometry of the thiocarbanion, as previously pointed out[4c,d] but has almost no effect on the stabilization energy SE. In fact, the main geometrical change associated with the inclusion of the sulfur 3d orbitals is a significant shortening of the C–S bond length, which becomes slightly shorter than that in the related monosubstituted methane. But, as pointed out above, a variation of the C–S bond length has only a minor effect upon the stabilization energy SE, since the two component terms SE(σ) and SE(NB) vary in opposite directions and with similar order of magnitude. Therefore, also when the sulfur 3d orbitals are included, the thiocarbanion is found to be more stabilized because of a σ effect.

We now attempt to understand in detail the mechanism of the σ effect on the basis of a one-electron MO(OEMO) model, where we consider the interactions of the hybrid orbitals which form the C–X bond in the anions and related monosubstituted methanes. The corresponding interactions diagram is shown in Figure 2. Here σ_O and σ_S denote the two singly occupied obritals of the –OH and –SH fragments involved in the formation of the C–O and C–S bonds, respectively, while σ_C and σ_{C^-} denote the singly occupied orbitals of carbon in the H_3C– and $H_2\bar{C}$– fragment, respectively.

The removal of a proton in the H_3C– fragment has two effects: a destabilization of the carbon hybrid orbital, so that σ_{C^-} is located at a significantly higher energy than σ_C, and a decrease of the

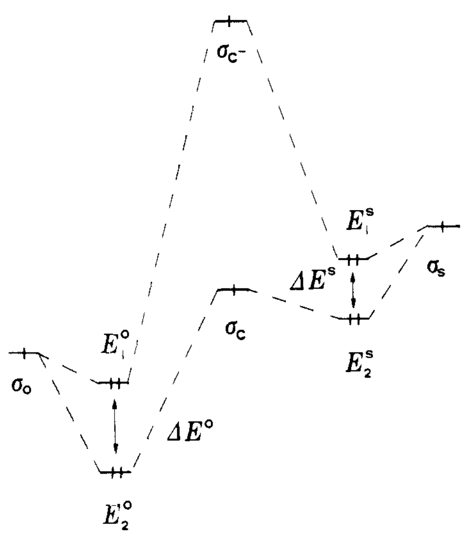

Figure 2. Diagram corresponding to the interaction between the singly occupied hybrid orbitals σ_O and σ_S and the singly occupied hybrid orbital σ_C (monosubstituted methane) or σ_{C^-} (anion) to form the σ_{C-X} doubly occupied central bond.

matrix element associated with the interaction of the two hybrid orbitals. Both effects concur to reduce the stabilization associated with the interaction of the two singly occupied orbitals in the anion compared to the related monosubstituted methane, with the variation of the matrix element playing the major role.

The bond weakening associated with the removal of a proton in the H_3C- fragment is more significant for X = OH than for X = SH, and this differential bond weakening effect is the source of the relative stability of the anions. In Figure 2 this effect is illustrated by the trend of the two quantities ΔE^O and ΔE^S, which represent, except for a constant, the substituent stabilization energies.

The result of the quantitative PMO analysis parallels the total energy results and shows that $\Delta E^O - \Delta E^S > 0$. The results of the PMO analysis show also that the factor responsible for this trend is the matrix element, which, in going from the monosubstituted methane to the corresponding anion, is reduced more in the oxy than in the thio derivatives. A different rationalization of the σ effect has been recently suggested by Larson and Epiotis in terms of a LCFC approach.[10]

Even if the nonbonded interactions do not play the dominant role, it can be of interest to analyze in detail their effects in order to clarify all aspects of the problem. The overall energy effects associated with the nonbonded interactions computed with the total energy approach and with the quantitative PMO analysis are listed in Table IV. The quantities $E_T - E_T{}^O$ denote the overall effect associated with the nonbonded interactions computed in terms of total energies and including also the effects associated with the inner orbitals. The quantities $\sum\Delta E^4$ denote the overall destabilizing contributions associated with the interactions between the doubly occupied fragment MO's, while $\sum\Delta E^2$ denotes the overall stabilizing contributions associated with the hyperconjugative interactions involving the doubly occupied MO's of one fragment and the vacant MO's of the other. Furthermore, $\sum\Delta E_{3d}{}^2$ denotes the stabilizing contribution associated with the interactions between the doubly occupied MO's of the $H_2\bar{C}$ fragment and the vacant sulfur 3d orbitals.

The analysis of these results shows the following: (i) the overall effect of the nonbonded interactions is destabilizing in all cases and more destabilizing in the oxy than in the thio derivatives. However, as previously pointed out, the variation of this effect in going from the methyl derivative to the anion is larger in the thio than in the oxy derivatives. (ii) the trend of the $\sum\Delta E^4$ values parallels well that of the $E_T - E_T{}^O$ values. In all cases the nonbonded repulsions increase going from H_3C-X to $H_2\bar{C}-X$ in the "frozen" geometry and then decrease going to the anion in the optimized geometry. (iii) the absolute magnitude of the stabilizing contributions $\sum\Delta E^2$ is larger in the oxy than in the thio derivatives, contrary to previous results.[6] (iv) the stabilizing contribution associated with the sulfur 3d orbitals is smaller than the hyperconjugative contribution and is larger in the anion than in the related methyl derivative.

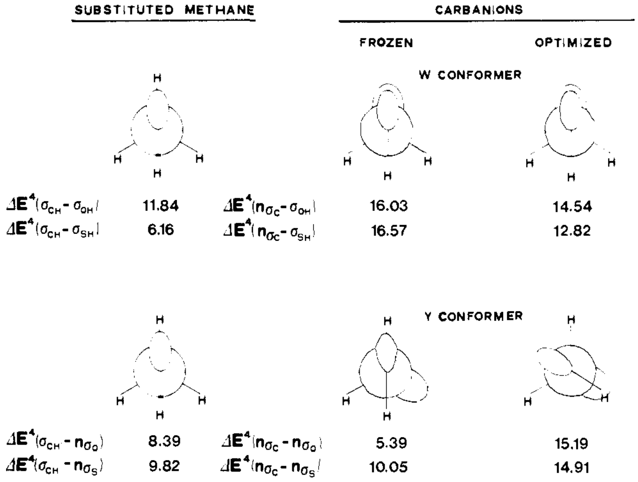

Figure 3. Relevant destabilizing interactions occurring in the substituted methanes and related carbanions.

As previously pointed out, the removal of the proton is accompanied by a significant increase of the destabilizing effect associated with the nonbonded interactions. In this process a bond orbital at a low-energy σ_{CH} ($\epsilon = -0.6964$ au) is replaced by a lone pair at a significantly higher energy n_{σ_C} ($\epsilon = -0.1249$). On the basis of the appropriate perturbation expression (see ref 13) it is easy to understand that this change in orbital energy determines a significantly larger ΔE^4 term in the anion. The interactions mainly affected are those with the largest overlap, which correspond in all cases to the anti interactions and are reported in Figure 3.

Also the trend of the stabilizing interactions deserves a comment. In a previous paper[6] it was assumed that the hyperconjugative interactions of the type $n_{\sigma_C}-\sigma_{XH}{}^*$ were more stabilizing in $H_2\bar{C}-SH$ than in $H_2\bar{C}-OH$ because of a smaller energy gap between the two interacting orbitals in the thio-substituted anion. The present quantitative analysis shows that, in addition to the $n_{\sigma_C}-\sigma_{XH}{}^*$ interactions, also the hyperconjugative interaction $\sigma_{CH}{}'-\sigma_{XH}{}^*$ can be significant. In particular, in the W conformer, the important interactions are $n_{\sigma_C}-\sigma_{XH}{}^*$ for X = O and $\sigma_{CH}{}'-\sigma_{XH}{}^*$ for X = S, with the former having the largest effect, while in the Y conformer the important interactions are $\sigma_{CH}{}'-\sigma_{XH}{}^*$ for X = O and $n_{\sigma_C}-\sigma_{XH}{}^*$ for X = S, with the former having the largest effect.

From the PMO results of Table IV it can be seen that the stabilizing effect associated with the sulfur 3d orbitals is small, so that the overall effect associated with the nonbonded interactions remains destabilizing also when the 3d orbitals are included. However, the 3d orbitals effect is sufficiently large to significantly modify the C–S stretching potential of the thiocarbanion, with the result that the minimum is shifted from values larger than 2 Å, computed in the absence of the 3d orbitals, to values of the order of 1.8 Å (see Table III) when the 3d orbitals are included.

More significant is the effect of the correlation energy corrections. The energy component of SE associated with this type of effect has been computed according to the following expression

$$\text{SE(CE)} = \text{SE(MP2/6-31+G*)} - \text{SE(6-31+G*)} \qquad (4)$$

where SE(MP2/6-31+G*) and SE(6-31+G*) denote the stabilization energies computed at the MP2/6-31+G* and 6-31+G* levels, respectively. The SE(CE) values for X = OH are 2.47 (W conformer) and 1.54 Kcal/mol (Y conformer), while for X = SH they are 9.32 (W conformer) and 9.31 Kcal/mol (Y conformer).

This type of energy component can be considered as a polarization effect arising from the low lying excited states involving, in addition to the d orbitals, also other types of empty orbitals

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such as σ_{C-X}^* and σ_{XH}^*. Since these empty orbitals are at lower energy when X = S, this effect favors the second-row substituent, as observed above.

4. Conclusion

In this paper we have attempted to rationalize the trends of the stabilization energies of the α-substituted oxy- and thiocarbanions $H_2\bar{C}{-}OH$ and $H_2\bar{C}{-}SH$. To this purpose we have decomposed the stabilization energies into the component terms associated with the σ-effects, the nonbonded interaction effects, the 3d-orbitals effects, and the correlation energy effects.

The analysis has shown that at all levels of computations investigated the SH group stabilizes the anionic center more than the OH group and that this trend is determined by the σ effects. An OEMO rationalization of this effect has shown that the stabilization energy of the SH group is larger because the bond weakening associated with the removal of a proton in the H_3C- fragment is more significant for X = OH than for X = SH. In turn, this trend is determined by the matrix element, which, in going from the monosubstituted methane to the related anion, is reduced more in the oxy than in the thio derivatives.

The analysis has shown also that the effect of the nonbonded interactions favors OH vs. SH and that the contribution of the sulfur 3d orbitals is very small. More significant appears to be the contribution associated with the correlation energy effects, which favors SH over OH.

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Catalysis of Electrochemical Reactions at Redox Polymer Coated Electrodes. Mediation of the Fe(III)/Fe(II) Oxido-Reduction by a Polyvinylpyridine Polymer Containing Coordinatively Attached Bisbipyridine Chlororuthenium Redox Centers

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Abstract: The [Ru(bpy)$_2$Cl-poly(4-vinylpyridine)] redox polymer catalyzes the oxidation of Fe(II) into Fe(III) in 1 M HCl in a quite efficient manner both in terms of current and potential. Quite substantial portions of the film thickness are active in the catalytic system, providing a good example of the interest of redox polymer coatings in the catalysis of electrochemical reactions as a result of the three-dimensional dispersion of the reacting centers. The polymer is also able to catalyze, although to a lesser extent, the reduction of Fe(III) to Fe(II) in the same medium in spite of the fact that the standard potential of the Ru(III)/Ru(II) couple is positive to that of the Fe(III)/Fe(II) couple. Analysis of the experimental data and the optimization of the catalytic efficiency by means of previously developed kinetic models demonstrate the validity of these models both in terms of the limiting currents and half-wave potentials featuring the catalytic process.

Redox polymer coated electrodes have been the object of active investigation during the past 10 years, motivated mainly by their applications to the catalysis of electrochemical reactions (for recent reviews see ref 2). The main reason for the interest they aroused in this respect is the expectation that they may combine the advantages of monolayer derivatized electrodes with those of homogeneous catalytic systems. With redox polymer coatings as with monolayer derivatized surfaces, high local concentrations of catalytic sites can be achieved even though the total amount of catalyst remains small. The two systems also share the advantage of an easy separability of the reaction products from the catalyst. On the other hand, redox polymer coatings, as homogeneous catalytic systems, offer a three-dimensional dispersion of the reacting centers as opposed to the two-dimensional arrangement prevailing at bare electrodes and at monolayer derivatized surfaces.[3] It follows that catalytic efficiencies of redox polymer coatings are expected to increase with the amount of redox polymer deposited on the electrode surface.[3] However, this potentiality may be counteracted by limitations imposed by the rates of substrate diffusion and charge propagation across the coatings. These may indeed be so severe that the catalytic reaction becomes a surface process occurring at either the coating–solution or the electrode–coating interfaces. Under such circumstances, monolayer derivatized surfaces may prove more efficient than redox

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[3] (a) This is the reason why catalysis can be obtained with redox polymer coatings and homogeneous systems, but not with monolayer derivatized surfaces, even in the cases where the catalyst simply exchanges electrons in an outer-sphere manner with the substrate.[3b,c] This "redox catalysis"[3d] thus results from physical rather than chemical reasons. In the case of "chemical catalysis",[3d–g] where an essential step is the transient formation of an adduct between the catalyst and the substrate, catalysis occurs at monolayer derivatized surfaces as a consequence of their particular chemical properties. The potential advantage of redox polymer coatings is then the possible multiplication of the effect as the number of equivalent monolayers of catalyst increases.[3b] (b) Andrieux, C. P.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *93*, 163. (c) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *Ibid.* **1981**, *123*, 171. (d) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *Ibid.* **1978**, *87*, 39. (e) Lexa, D.; Savéant, J. M.; Soufflet, J. P. *Ibid.* **1979**, *100*, 159. (f) Anson, F. C.; Ni, C. L.; Savéant, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 3442. (g) Lexa, D.; Savéant, J. M.; Wang, D. L. *Organometallics* **1986**, *5*, 7428.

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