Russian Chemical Bulletin, International Edition, Vol. 56, No. 8, pp. 1481—1486, August, 2007

Full Articles

The sulfonation of pyrrole: choice of relevant computational procedure for quantum chemical analysis of positional orientation*

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The influence of the solvent effect, zero-point energy correction, and electron correlation on conclusions about positional orientation of pyrrole sulfonation was studied by the B3LYP, HF, and MP2 methods with the 6-31G(d) and 6-31+G(d) basis sets. The most important role is played by the solvation effects. Basis set extension effects and the inclusion of zero-point energy correction contribute insignificantly. According to calculations using all the methods listed above, the formation of β-pyrrolesulfonic acid in polar solvent is thermodynamically more favorable and less kinetically hindered. B3LYP calculations seem to be more appropriate, because the method allows experimental data on positional orientation of the sulfonation of pyrroles to be interpreted in a simpler and more reliable fashion.

Key words: quantum chemical calculations; B3LYP, HF, and MP2 methods; 6-31G(d) and 6-31+G(d) basis sets; pyrrole sulfonation; positional selectivity of substitution.

Contrary to the available data on preferred formation of α-isomers in the electrophilic substitution of five-membered heteroaromatic compounds containing one heteroatom,[1] the sulfonation of pyrrole and *N*-methylpyrrole with pyridine—sulfur trioxide complex results in β-sulfonic acids as sole products.[2] Recently,[3—5] we have considered the sulfonation reaction mechanism using a simple model for the interaction of SO_3 and pyrrole molecules, which involves the formation of the α- and β-isomers (**A** and **B**, respectively) of the σ-complex (Scheme 1) as the first stage followed by intramolecular rearrangement of the isomers to the corresponding isomeric sulfonic acids (Scheme 2).

The isomers **A** and **B** of the intermediate σ-complex can undergo interconversion owing to reversibility of the first stage (see Scheme 1) or as a result of the α,β-migration of sulfonic group (Scheme 3).

The α-isomer **A** is energetically more favorable, which is well known for similar σ-complexes formed in the reactions of electrophilic substitution in five-membered heterocycles[1] and can be explained by the possibility of more efficient delocalization of the positive charge in the ring attacked by an electrophile at the α-position. How-

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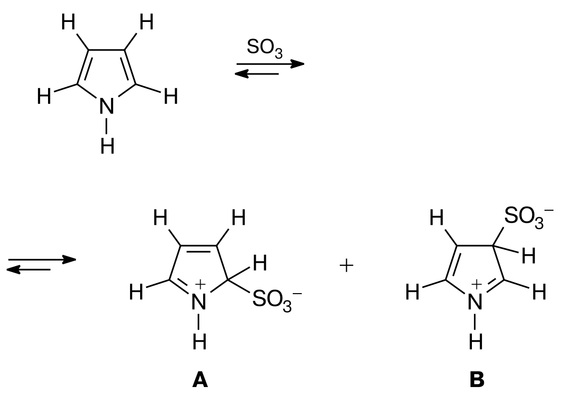
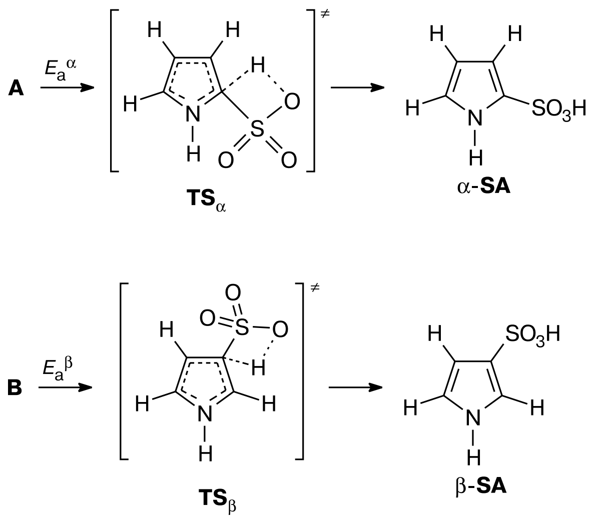
* Dedicated to Academician V. A. Tartakovsky on the occasion of his 75th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1425—1430, August, 2007.

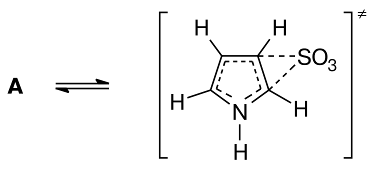
Scheme 1



Scheme 2



Scheme 3



ever, this provides no unambiguous proof of preferred formation of the α-isomer of the product. Indeed, despite preponderance of the more stable α-isomer in the hypothetical equilibrium mixture of the **A** and **B** isomers the formation of products occurs in the second stage, and β-sulfonic acid, which is energetically more preferable, can form faster.

The formation of sulfonic acids in the course of intramolecular rearrangements of the σ-complexes **A** and **B** occurs through transfer of a proton from the carbon atom bonded to the sulfonic group to an oxygen atom of the sulfonic group (see Scheme 2). According to B3LYP/6-31G(d) calculations,[4,5] in a polar solvent at a rather small energy difference between isomeric transition states $\mathbf{TS}_\alpha$ and $\mathbf{TS}_\beta$ the barrier to rearrangement of the intermediate **A** is higher than for the isomer **B** ($E_a^\alpha > E_a^\beta$) (Fig. 1).

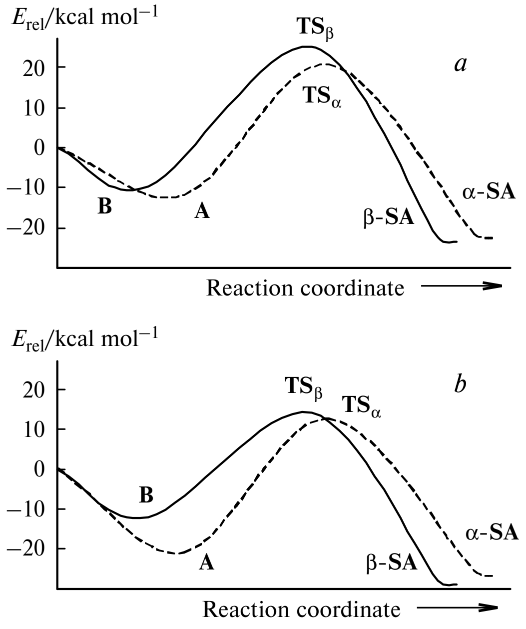


Fig. 1. Energy profiles of alternative routes of the reaction of pyrrole sulfonation obtained from B3LYP/6-31G(d) calculations.[2] The energies of the systems (E_{rel}, kcal mol^{-1}) were calculated relative to the total energy of isolated pyrrole and SO_3 molecules in the gas phase (*a*) and in methylene chloride (*b*).

This provides an explanation for preferred formation of β-pyrrolesulfonic acid at particular energy ratios for the isomers **A** and **B**, transition states $\mathbf{TS}_\alpha$ and $\mathbf{TS}_\beta$, and products of the interaction of pyrrole with SO_3 (see Refs 4 and 5). These ratios can strongly depend on particular methods employed for quantum chemical calculations. In this work we analyze how limitations accepted earlier[4,5] affect the conclusions about orientation of the reaction of pyrrole sulfonation.

Results and Discussion

Table 1 lists the relative energies of isomers **A** and **B** (E_{int}), transition states $\mathbf{TS}_\alpha$ and $\mathbf{TS}_\beta$ (E_{TS}), and reaction products, that is, sulfonic acids α-**SA** and β-**SA** (E_{prod}) obtained from B3LYP and HF calculations. All calculations were carried out with full geometry optimization with the 6-31G(d) and 6-31+G(d) basis sets, as well as with and without inclusion of zero-point energy corrections and the effect of the model solvent (methylene chlo-

Table 1. Relative energies (kcal mol^{-1}) of the isomeric intermediates **A** and **B** (E_{int}), transition states $\mathbf{TS}_{\alpha}$ and $\mathbf{TS}_{\beta}$ (E_{TS}), and pyrrolesulfonic acids α-**SA** and β-**SA** (E_{prod})*

Row	Method**	$-E_{\text{int}}^{\alpha}$	$-E_{\text{int}}^{\beta}$	E_{TS}^{α}	E_{TS}^{β}	$-E_{\text{prod}}^{\alpha}$	$-E_{\text{prod}}^{\beta}$
				Gas phase			
1	B3LYP/6-31G(d), *A*	11.8	9.6	20.7	25.3	21.5	22.3
2	B3LYP/6-31G(d), *B*	10.0	8.4	19.7	24.1	19.7	20.6
3	B3LYP/6-31+G(d), *A*	9.9	7.5	23.3	27.4	19.9	21.0
4	B3LYP/6-31+G(d), *B*	8.1	6.3	22.2	26.1	18.1	19.3
				Solvent CH_2Cl_2			
5	B3LYP/6-31G(d), *A*	20.9	12.0	12.5	14.2	25.6	28.0
6	B3LYP/6-31G(d), *B*	18.9	13.6	11.3	13.7	24.0	26.5
7	B3LYP/6-31+G(d), *A*	20.5	14.8	14.5	16.6	24.3	26.7
8	B3LYP/6-31+G(d), *B*	18.6	13.1	13.3	15.3	22.6	25.2
				Gas phase			
9	HF/6-31G(d), *A*	12.9	4.0	32.9	35.2	27.3	29.9
10	HF/6-31G(d), *B*	10.2	1.8	31.9	34.1	25.1	27.8
11	HF/6-31+G(d), *A*	11.7	2.7	34.8	36.7	25.8	28.5
12	HF/6-31+G(d), *B*	9.1	0.5	33.7	35.6	23.7	26.4
				Solvent CH_2Cl_2			
13	HF/6-31G(d), *A*	30.2	22.6	23.4	22.8	31.8	35.9
14	HF/6-31G(d), *B*	27.5	20.0	22.4	21.7	29.8	34.2
15	HF/6-31+G(d), *A*	29.4	21.9	25.2	24.3	30.4	34.8
16	HF/6-31+G(d), *B*	27.0	19.7	23.9	23.0	28.6	33.0
				Gas phase			
17	MP2//HF/6-31G(d)	8.0	3.0	21.3	25.7	25.8	26.6
				Solvent CH_2Cl_2			
18	MP2//HF/6-31G(d)	20.3	−14.1	14.3	14.7	30.0	32.4

* In all cases (rows *1—18*) the energies are given relative to the total energy of isolated pyrrole and SO_3 molecules calculated for the particular row.

** Notations: *A* and *B* respectively denote calculations without and with inclusion of zero-point energy correction.

ride, using the model of overlapping spheres) using the GAUSSIAN-98[6] program. The HF/6-31G(d) computed energies of the structures in the gas phase and in the model solvent were refined at the MP2/6-31G(d) level of perturbation theory without additional geometry optimization. All energies were calculated relative to the total energy of the reactant molecules, pyrrole and SO_3.

Table 2 lists the energy differences $\Delta E_{\text{X}} = E_{\text{X}}^{\alpha} - E_{\text{X}}^{\beta}$ ($E_{\text{X}} = E_{\text{int}}, E_{\text{TS}}, E_{\text{prod}}$) between the isomers **A** and **B**, transition states, and reaction products. The ΔE_{X} values characterize the energy preferableness of the α- ($\Delta E_{\text{X}} < 0$) or β-isomer ($\Delta E_{\text{X}} > 0$). The activation energies (E_{a}) for rearrangements of the isomeric intermediates and the activation energy differences $\Delta E_{\text{a}} = (E_{\text{a}}^{\alpha} - E_{\text{a}}^{\beta})$, which point to the energy preferableness of rearrangement of the α- ($\Delta E_{\text{a}} < 0$) or β-intermediate ($\Delta E_{\text{a}} > 0$), are also included in Table 2. The ΔE_{a} is defined in two manners, namely, as the activation energy difference between the rearrangements of the isomeric intermediates and as the difference of the energy differences between corresponding isomeric transition states and intermediates:

$$\Delta E_{\text{a}} = E_{\text{a}}^{\alpha} - E_{\text{a}}^{\beta} = (E_{\text{TS}}^{\alpha} - E_{\text{int}}^{\alpha}) - (E_{\text{TS}}^{\beta} - E_{\text{int}}^{\beta}) =$$
$$= (E_{\text{TS}}^{\alpha} - E_{\text{TS}}^{\beta}) - (E_{\text{int}}^{\alpha} - E_{\text{int}}^{\beta}) = \Delta E_{\text{TS}} - \Delta E_{\text{int}}.$$

In the text below we will analyze the results of our calculations with the most detailed consideration of the B3LYP data obtained earlier.[3—5]

Gas-phase calculations with inclusion of zero-point energy correction

According to our gas-phase B3LYP/6-31G(d) calculations without inclusion of zero-point energy correction,[2] the formation of the α-isomer **A** having a lower relative energy than the β-isomer **B** in the first stage of the reaction is energetically more favorable (see Table 1, row *1*). Analysis of the second stage of the gas-phase reaction showed that the transition state $\mathbf{TS}_{\alpha}$ is also more favorable than $\mathbf{TS}_{\beta}$, the energy difference ΔE_{TS} being larger in absolute value than the energy difference ΔE_{int} between intermediates **A** and **B** (see Table 2, row *1*). Therefore, the activation energy for rearrangement of the α-isomer **A** is lower than that required for rearrangement of the β-isomer **B** (see Fig. 1, *a*). However, the reverse was found for products, pyrrolesulfonic acids, for which the β-isomer is more stable (see Table 1, row *1*).

The inclusion of zero-point energy correction in gas-phase B3LYP/6-31G(d) calculations causes the relative

Table 2. Energy differences $\Delta E_X = E_X{}^{\alpha} - E_X{}^{\beta}$ between the isomeric intermediates **A** and **B** (ΔE_{int}), transition states $\mathbf{TS}_{\alpha}$ and $\mathbf{TS}_{\beta}$ (ΔE_{TS}), and pyrrolesulfonic acids α-**SA** and β-**SA** (ΔE_{prod}), the activation energies $E_a{}^{\alpha}$ and $E_a{}^{\beta}$ for rearrangements of isomers **A** and **B**, and the activation energy differences $\Delta E_a = (E_a{}^{\alpha} - E_a{}^{\beta})$

Row	Method*	$-E_{int}$	ΔE_{TS}	ΔE_{prod}	$E_a{}^{\alpha}$	$E_a{}^{\beta}$	ΔE_a
		kcal mol^{-1}					
Gas phase							
1	B3LYP/6-31G(d), *A*	2.2	−4.6	0.8	32.5	34.9	−2.4
2	B3LYP/6-31G(d), *B*	1.6	−4.4	0.9	29.6	32.5	−2.9
3	B3LYP/6-31+G(d), *A*	2.4	−4.1	1.1	33.2	34.9	−1.7
4	B3LYP/6-31+G(d), *B*	1.8	−3.9	1.2	30.3	32.4	−2.1
Solvent CH_2Cl_2							
5	B3LYP/6-31G(d), *A*	8.9	−1.7	2.4	33.5	26.2	7.3
6	B3LYP/6-31G(d), *B*	5.3	−2.4	2.5	30.2	27.3	2.9
7	B3LYP/6-31+G(d), *A*	5.7	−2.1	2.4	35.1	31.4	3.7
8	B3LYP/6-31+G(d), *B*	5.5	−2.0	2.6	31.9	28.3	3.6
Gas phase							
9	HF/6-31G(d), *A*	8.9	−2.3	2.6	45.8	39.2	6.6
10	HF/6-31G(d), *B*	8.4	−2.2	2.7	42.1	35.9	6.2
11	HF/6-31+G(d), *A*	9.0	−1.9	2.7	46.4	39.4	7.0
12	HF/6-31+G(d), *B*	8.6	−1.9	2.7	42.8	36.1	6.7
Solvent CH_2Cl_2							
13	HF/6-31G(d), *A*	7.6	0.6	4.1	53.6	45.3	8.3
14	HF/6-31G(d), *B*	7.5	0.7	4.3	49.9	41.8	8.1
15	HF/6-31+G(d), *A*	7.5	0.9	4.4	54.6	46.1	8.5
16	HF/6-31+G(d), *B*	7.3	0.9	4.4	50.9	42.6	8.3
Gas phase							
17	MP2//HF/6-31G(d)	5.0	−4.4	0.8	29.3	28.7	0.6
Solvent CH_2Cl_2							
18	MP2//HF/6-31G(d)	6.2	−0.4	2.4	34.6	28.8	5.8

* Notations: *A* and *B* respectively denote calculations without and with inclusion of zero-point energy correction.

energies of the isomeric intermediates **A** and **B** and the α- and β-pyrrolesulfonic acids to increase to some extent, whereas the relative energies of transition states $\mathbf{TS}_{\alpha}$ and $\mathbf{TS}_{\beta}$ decrease (see Table 1, row *2*). Correspondingly, the activation energies for rearrangements somewhat decrease (see Table 2, row *2*).

Noteworthy is that the energy differences between the isomeric intermediates, transition states, and products, as well as the activation energies for rearrangements change for each pair of isomers in parallel within 0.1—0.6 kcal mol^{-1} (see Table 2, rows *1* and *2*). Therefore, in this case the conclusions drawn earlier[4] remain essentially the same (see Fig. 1, *a*).

Gas-phase calculations: basis set extension effects

Gas-phase B3LYP calculations with the 6-31+G(d) basis set augmented with diffuse functions for non-hydrogen atoms give slightly higher relative energies of isomers **A** and **B**, transition states $\mathbf{TS}_{\alpha}$ and $\mathbf{TS}_{\beta}$, and products α-**SA** and β-**SA** (see Table 1, row *3*). The energy differences for corresponding pairs isomers also change insignificantly (see Table 2, row *3*), *i.e.*, the general pattern remains the same (see Fig. 1, *a*) as in the previous case (see Table 2, rows *1—3*).

Gas-phase calculations with inclusion of zero-point energy correction and diffuse functions

Gas-phase B3LYP calculations with the 6-31+G(d) basis set and inclusion of zero-point energy correction cause the relative energies of isomeric intermediates **A** and **B**, transition states $\mathbf{TS}_{\alpha}$ and $\mathbf{TS}_{\beta}$, and products α-**SA** and β-**SA** to increase in parallel (see Table 1, rows *1* and *4*). The energy differences between corresponding pairs of isomers also increase in parallel by 0.3—0.5 kcal mol^{-1} (see Table 2, rows *1* and *4*). Thus, the overall pattern of the energy ratios for corresponding isomeric forms (see Fig. 1, *a*) in the case of gas-phase B3LYP calculations remain almost unchanged.

Calculations with allowance for solvation effects

The B3LYP/6-31G(d) calculated relative energies of the isomeric intermediates **A** and **B**, transition states $\mathbf{TS}_{\alpha}$ and $\mathbf{TS}_{\beta}$, and pyrrolesulfonic acids α-**SA** and β-**SA** obtained with allowance for the effect of the model solvent (CH_2Cl_2) are appreciably different from the corresponding values found in gas-phase calculations (see Table 1, rows *1* and *5*). All energies decrease upon inclusion of solvation effects, the changes being most pronounced for the α-intermediate **A** and both isomeric transition states $\mathbf{TS}_\alpha$ and $\mathbf{TS}_\beta$ (see Table 1). Considering corresponding pairs of isomers, the energies of the α-intermediate **A**, transition state $\mathbf{TS}_\beta$, and β-sulfonic acid decrease to a greater extent, thus leading to significant changes in the energy ratios of the isomeric forms (see Table 2, rows *1* and *5*). Namely, the energy difference between isomers **A** and **B** becomes much larger than between the transition states $\mathbf{TS}_\alpha$ and $\mathbf{TS}_\beta$. As a consequence, the activation energy difference ΔE_a changes its sign and the rearrangement of the β-intermediate **B** becomes more preferable.

The activation energy for rearrangement of the α-intermediate **A** changes only slightly, because taking account of solvation effect causes an almost identical decrease in the relative energies of the isomer **A** and transition state of its rearrangement, $\mathbf{TS}_\alpha$. The activation energy for rearrangement of isomer **B** considerably decreases because the energy of this species decreases to a much smaller extent upon inclusion of solvation effects compared to the energy of the corresponding transition state $\mathbf{TS}_\beta$. The energy preference of the β-isomer of pyrrolesulfonic acid (β-**SA**) increases in solution (see Table 1, rows *1* and *5*).

The overall pattern of the energy ratios for the isomeric forms under study in the model solvent (CH_2Cl_2) is illustrated by Fig. 1, *b*.

Calculations with inclusion of zero-point energy correction and solvation effects

Similarly to the gas-phase computations (see Table 1, rows *1* and *2*) the B3LYP/6-31G(d) calculations with inclusion of zero-point energy correction and the effect of the model solvent (see Table 1, row *6*) predict a decrease in the relative energies of the isomeric transition states $\mathbf{TS}_\alpha$ and $\mathbf{TS}_\beta$ and an increase in the relative energies of both pyrrolesulfonic acids and the α-intermediate **A**. In addition, the relative energy of the β-intermediate **B** decreases rather than increases as in the case of gas-phase calculations (see Table 1). As a consequence, the energy difference between isomers **A** and **B** noticeably changes, now characterizing a lower energy preferableness of the α-isomer **A**. This eventually leads to a decrease in the activation energy difference ΔE_a (see Table 2, rows *5* and *6*) because the transition state $\mathbf{TS}_\alpha$ becomes somewhat more preferable than $\mathbf{TS}_\beta$. The activation energy for rearrangement decreases for the α-intermediate **A** and increases for the β-isomer, whereas the energy difference between the isomeric products, ΔE_{prod}, remains almost unchanged.

According to calculations, the activation energy difference changes in such a manner that rearrangement of the β-isomer **B** becomes less favorable. In spite of this, taking account of zero-point energy correction in B3LYP/6-31G(d) calculations with allowance for the effect of the model solvent (see Table 2, row *6*) does not change the qualitative conclusions drawn earlier[4] (see Fig. 1, *b*).

Calculations with inclusion of solvation effects and extended basis set

As in the case of gas-phase calculations (*cf.* rows *1* and *3*), the relative energies of the isomeric transition states and products increase on going from the 6-31G(d) basis set (see Table 1, row *5*) to the 6-31+G(d) basis set (Table 1, row 7). But unlike the results obtained for the gas phase the relative energy of the α-intermediate **A** in solvent remains almost unchanged while that of the β-isomer **B** decreases. Changes in the energy differences between corresponding isomeric forms upon extension of the basis set and allowance for the solvation effect (see Table 2, row *7*) are similar to the changes upon applying zero-point energy correction (see Table 2, row *6*). It follows that extension of the basis set also has no effect on the qualitative results obtained earlier.[4]

Calculations with solvation effects, zero-point energy correction, and diffuse functions included

B3LYP calculations with the extended basis set and inclusion of zero-point energy correction (see Table 1, row *8*) predict changes in the relative energies of the starting solvated α- and β-isomers **A** and **B** (see Table 1, row *5*) in opposite directions, as if extension of the basis set or introduction of zero-point energy correction were done separately (see Table 1, rows *6* and *7*). The energies of the isomeric transition states $\mathbf{TS}_\alpha$ and $\mathbf{TS}_\beta$ and sulfonic acids increase (see Table 1, row *8*) similarly to the gas-phase computations (see Table 1, rows *1* and *4*).

By and large, comparison of the energy characteristics of corresponding pair isomers in the gas phase (see Table 1 and 2; rows *1—4*) and in the model solvent CH_2Cl_2 (see Table 1 and 2; rows *5—8*) shows that it is the inclusion of solvation effects in the B3LYP calculations that is responsible for the qualitative changes and corresponding conclusions[4] about the effect of the solvent on positional orientation of the reaction of pyrrole sulfonation illustrated by Fig. 1, whereas extension of the basis set and taking account of zero-point energy correction only slightly influence quantitative characteristics.

Hartree—Fock calculations with inclusion of electron correlation

The relative energies of the isomeric intermediates **A** and **B**, transition states $\mathbf{TS}_\alpha$ and $\mathbf{TS}_\beta$, and pyrrolesulfonic acids α-**SA** and β-**SA** obtained from gas-phase HF/6-31G(d) calculations without inclusion of zero-point energy correction (see Table 1, row *9*) are strongly different (except the α-intermediate **A**) from the corresponding B3LYP computed values (see Table 1, row *1*). Namely, the relative energies of the β-isomer **B**, isomeric transition states $\mathbf{TS}_\alpha$ and $\mathbf{TS}_\beta$, and pyrrolesulfonic acids α-**SA** and β-**SA** and activation energies $E_a{}^\alpha$ and $E_a{}^\beta$ for rearrangements of the isomeric intermediates **A** and **B** considerably increase. With the qualitative pattern of the relative energy levels retained, the energy difference between the transition states $\mathbf{TS}_\alpha$ and $\mathbf{TS}_\beta$ decreases while the energy difference between the products, α-**SA** and β-**SA**, increases. Too high activation barriers $E_a{}^\alpha$ and $E_a{}^\beta$ favor a rearrangement of the β-isomer rather than α-intermediate in the gas phase (*cf.* rows *1* and *9* in Tables 1 and 2).

Similarly to the B3LYP calculations, extension of the basis set and inclusion of zero-point energy correction in the Hartree—Fock case have almost no effect on the ratios of the energy characteristics of the isomeric forms (see Table 2, rows *10—12* and *14—16*), whereas the inclusion of solvation effects causes a significant decrease in their relative energies (see Table 1, rows *13—16*). Even higher activation energies, $E_a{}^\alpha$ and $E_a{}^\beta$, for rearrangements of the solvated intermediates **A** and **B**, through the energy differences ΔE_a provide a qualitative indication of increased preferableness of the β-route to β-pyrrolesulfonic acid. This also follows from the increased relative energy differences, ΔE_{prod}, between products (see Table 2, rows *13—16*).

The inclusion of electron correlation energy at the MP2 level of perturbation theory for the HF/6-31G(d)-optimized structures under study in the gas phase and in the model solvent leads to marked increase in the relative energies of the intermediates **A** and **B**, as well as α- and β-pyrrolesulfonic acids and to a decrease in the relative energies of the transition states $\mathbf{TS}_\alpha$ and $\mathbf{TS}_\beta$ (see Table 1, *cf.* rows *9* and *17*, *13* and *18*). The activation energies for rearrangements of the intermediates considerably decrease (see Table 2, rows *9* and *17*, *13* and *18*).

The energies of the corresponding isomeric pairs do not change in parallel upon inclusion of correlation corrections and the ratios of the differences between the refined energies become significantly different (see Table 2, rows *9* and *17*, *13* and *18*), especially for the gas phase. Namely, the relative energy preferableness of the α-intermediate **A** (ΔE_{int}) and β-pyrrolesulfonic acid (ΔE_{prod}) decreases appreciably while the transition state $\mathbf{TS}_\alpha$ (ΔE_{TS}) becomes more favorable. As a consequence, the activation energy difference, ΔE_a, between the rearrangements of the isomeric intermediates becomes smaller than, being equal to almost zero for the gas phase. Taking into account a decrease in the relative energy preferableness of β-pyrrolesulfonic acid, this indicates that the energy differences between the α- and β-routes of the reaction of pyrrole sulfonation in the gas phase almost vanish, whereas the β-route remains more preferable in the model solvent.

Thus, the results of our B3LYP quantum chemical calculations show that the effect of the polar solvent is the key factor responsible for the preferred formation of β-pyrrolesulfonic acid. The basis set extension effects and inclusion of zero-point energy correction contribute insignificantly. This is also indicated by the results of the HF calculations. In addition, the decisive role played by the effect of the polar solvent on the orientation of the reaction of pyrrole sulfonation follows from the results of Hartree—Fock calculations with inclusion of electron correlation energy at the MP2/6-31G(d) level of theory.

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Received June 7, 2007