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Theoretical Studies on the Base-Catalyzed Deprotonation of Sulfonyl-Activated Carbon Acids

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Theoretical AM1 MO studies are reported on the gas-phase deprotonations of N-methyl 4-((Y-phenylsulfonyl) pyridinium cations (**IV**) and N-(Y-benzyl) 4-((phenylsulfonyl)methyl pyridinium cations (**V**) using NH_3 as a base. Brönsted α values for deprotonation of **IV** and **V** are 0.18 and 0.17, respectively. Brönsted β value of 0.53 is found for the deprotonation of **IV** and **V** by substituted aniline bases. The negative transition state (TS) imbalances, I ($=\alpha-\beta$)<0, are rationalized by the negative distance factor, Δd ($=d_p-d_{TS}$)<0, where d_p and d_{TS} are the distance between anionic charge center and substituents in the product and in the TS, respectively. The inability of d-$p\pi$-conjugation in **IV**, where instead n-σ^* type sigma delocalization occurs, causes very little lag in the structural reorganization in the TS.

Introduction

Transition state (TS) imbalances are a common phenomenon in many chemical reactions including proton transfers involving activated carbon acids.[1] Such imbalances have been formulated as a rule by Bernasconi, called the principle of nonperfect synchronization (PNS).[2] The PNS asserts that whenever resonance (and/or solvation) is involved as product (or reactant) stabilizing factor in a reaction, this factor will develop late (or be lost early) in the transition state.[2] In the proton transfers the TS imbalance (I) is expressed as $I=\alpha_{CH}-\beta_B$, where α_{CH} is the Brönsted coefficient obtained by varying the pK_a of the carbon acid and β_B is obtained by varying the pK_a of the base (amine or oxyanion).

The I value is in most cases positive, but in some cases the sign of I becomes negative.[1e,2]

In a previous work,[3] we have shown theoretically that the negative I values for the base catalyzed deprotonations of 1-methyl-4-(Y-phenacyl)pyridinium, **I** ($R^1=Y-C_6H_4-$ and $R^2=CH_3$ in Scheme 1), and 1-benzyl-4-(Y-phenacyl)pyridinium, **II** ($R^1=C_6H_5-$ and $R^2=Y-C_6H_4-CH_2-$ in Scheme 1), cations
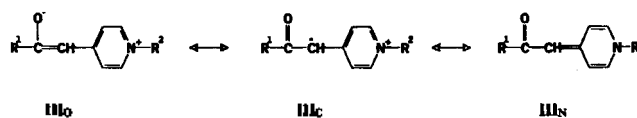

Scheme 1.

Table 1. Heats of formation (ΔH_f) of the stationary point species, activation parameters ($\Delta H^{\neq}$, $-T\Delta S^{\neq}$, $\Delta G^{\neq}$) and reaction energies (ΔH°, $-T\Delta S^{\circ}$, ΔG°) in kcal mol^{-1} for the deprotonation of cations IV and V with NH_3

Cation	Y	ΔH_f					Acivation Parameters			Reaction Energies		
		R	RC	TS	PC	P	$\Delta H^{\neq}$	$-T\Delta S^{\neq a}$	$\Delta G^{\neq a}$	ΔH°	$-T\Delta S^{\circ}$	ΔG°
(IV)	p-OCH$_3$	100.0	94.7	97.9	77.2	1121.6	-2.1	11.2	9.1	21.6	-0.3	21.3
	p-CH$_3$	132.0	126.5	129.6	108.8	152.8	-2.4	11.3	8.9	20.8	0.0	20.8
	H	140.8	135.3	138.2	117.2	160.7	-2.6	11.2	8.6	19.9	-0.1	19.8
	p-CN	177.4	171.7	174.0	152.5	192.7	-3.4	11.2	7.8	15.3	-0.1	15.2
	p-NO$_2$	153.6	147.7	149.6	127.5	165.0	-4.0	11.2	7.2	114	-0.2	11.2
(V)	p-OCH$_3$	125.8	120.6	134.2	105.0	149.9	-1.6	11.1	9.5	24.1	-0.6	23.5
	p-CH$_3$	156.5	151.2	154.8	135.4	180.2	-1.7	11.2	9.5	23.7	-0.2	23.5
	H	165.0	159.6	163.1	143.5	188.0	-1.9	11.1	9.2	23.0	-0.2	22.8
	p-CN	201.0	195.5	198.8	178.0	220.6	-2.2	11.0	8.8	19.6	-0.3	19.3
	p-NO$_2$	176.6	171.0	174.1	152.2	193.5	-2.5	10.8	8.3	16.9	-0.1	16.8

^{a} At 298 K.

are largely due to the greater distance (d_{TS}) between the substituents (Y) and the negative charge developed in the TS, III_C, than in the product anion (d_P), III_O or III_N, i.e., the negative Δd ($=d_P-d_{TS}<0$) leads to the negative I ($=\alpha_{CH}-\beta_B<0$).

In recent studies, Wodzinski and Bunting[4] have shown that similar negative I values are also observable in aqueous solution at 25 °C for the deprotonations of two series of sulfones (IV and V) which are close structural analogs of the ketonic carbon acids I and II.[5] In order to compare substituent effects and TS structure, including the imbalance behaviors, for the deprotonation of such closely related sulfones and ketones, we have carried out in this work similar theoretical analyses of the factors determining the TS imbalances involved in the gas-phase deprotonations of IV and V.
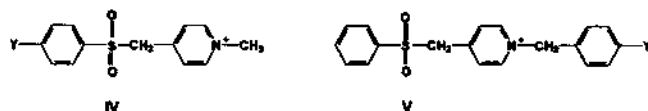
Calculations

The semiempirical MO method, AM1,[6] was used throughout in this work. All stationary point structures including TSs were fully optimized and were characterized by harmonic vibrational frequency calculations.[7] Entropy changes were also calculated to obtain Gibbs free energies of reaction, ΔG°, and of activation, $\Delta G^{\neq}$. Computations were performed using the MOPAC 6.0 program package.[8]

Results and Discussion

The relevant energetic data for the base catalyzed deprotonation of cations IV and V using NH_3 as a base are summarized in Table 1. The trends of substituent effects on the rates (or on $\Delta G^{\neq}$) are quite similar to those of the corresponding reactions I and II.[3] Here again, the entropy effects vary little depending on the substituents Y. The gas-phase Brönsted α coefficients are obtained by eq. (1), using the proton affinities (PA) of VI_C (Scheme 2) calculated with the AM1 method (Table 2). The α values determined are α_{SO} (for IV with the product structure VI_O)=0.18 (r=0.993) and α_{SN} (for V with the product structure VI_N)=0.17 (r=

Table 2. Proton affinities (ΔPA in kcal mol^{-1})^a of the conjugate bases of cations IV and V

Y	IV	V
p-OCH$_3$	1.5	0.7
p-CH$_3$	1.0	0.7
H	0.0	0.0
p-CN	-4.6	-3.5
p-NO$_2$	-8.6	-6.0

^{a} HA $\rightleftarrows$ H$^+$+A$^-$, ΔPA=PA(Y)$-$PA(H) : PA of Y=H is 26.8 and 29.9 kcal mol^{-1} for (IV) and (V), respectively (in this case, PA is calculated excepting the Gibbs energy of H$^+$).
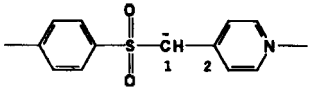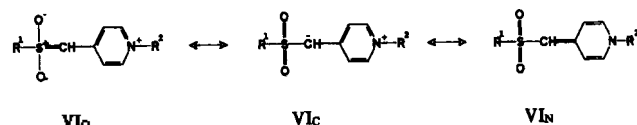

Scheme 2.

0.98$_7$). The same α values are also obtained by the Leffler-Hammond plots,[9] eq. (2), and by the normalized ρ_{kin}, ($\alpha=\rho_n=$ ρ_{kin}/ρ_{eq}).[10] The ρ values were ρ_{kin}=0.91 (r=0.996) and $\rho_{eq}=$ 4.97 (r=0.999) for V and ρ_{kin}=0.58 (r=0.993) and ρ_{eq}=3.43 (r=0.997) for VI respectively. Obviously, longer distance between the substituent (Y) and the anionic charge center involved in V causes to lower the ρ_{kin} and ρ_{eq} values relative to the corresponding values for IV.

$$\delta\Delta G^{\neq} = \alpha \cdot \delta(PA) \tag{1}$$

$$\delta\Delta G^{\neq} = \alpha \cdot \delta\Delta G^{\circ} \tag{2}$$

Experimentally in aqueous solution, the α_{SO} values observed are 0.59 and 0.45 with bases OH$^-$ (pK_a=15.74) and CO_3^{2-} (pK_a=10.04) respectively, while the corresponding α_{SN} values are 0.33 and 0.29 for the two bases.[4] Thus the AM1 gas-phase α values are smaller than those corresponding experimental values. Comparing with the α values obtained using the CO_3^{2-} ion base, which has the pK_a closer to that of the base used (NH_3) in the present work (pK_a for NH_4^+ is 9.24), the experimental α values in aqueous solution are considered to be higher by 0.27 ($\Delta\alpha_{SO}=$ 0.45-0.18) and 0.12 ($\Delta\alpha_{SN}$=0.29-0.17) than the corresponding gas-phase AM1 values. The higher experimental

Table 3. Some calculated bond lengths (Å) for the deprotonation of cations **IV** and **V** with NH_3

| Y		IV		V	
		$l(C_1\text{-}S)$	$l(C_1\text{-}C_2)$	$l(C_1\text{-}S)$	$l(C_1\text{-}C_2)$
p-OCH$_3$	R	1.779	1.468	1.770	1.471
	TS	1.710	1.436	1.700	1.438
	P	1.624	1.362	1.621	1.363
	%Δl$^{\pm a}$	4.5%	30.2%	47.0%	30.6%
p-CH$_3$	R	1.777	1.469	1.770	1.470
	TS	1.709	1.437	1.700	1.438
	P	1.624	1.362	1.622	1.363
	%Δl$^{\pm a}$	44.4%	29.9%	47.3%	29.9%
H	R	1.775	1.469	1.771	1.470
	TS	1.708	1.438	1.701	1.438
	P	1.623	1.363	1.622	1.363
	%Δl$^{\pm a}$	44.1%	29.2%	47.0%	29.9%
p-CN	R	1.770	1.470	1.773	1.470
	TS	1.705	1.440	1.705	1.438
	P	1.616	1.365	1.626	1.362
	%Δl$^{\pm a}$	42.2%	28.6%	46.3%	29.6%
p-NO$_2$	R	1.766	1.471	1.775	1.469
	TS	1.702	1.443	1.709	1.438
	P	1.610	1.367	1.629	1.361
	%Δl$^{\pm a}$	41.0%	26.9%	46.3%	28.7%

^{a} %Δl$^{\pm}$=100 · $(l_{TS}\text{-}l_R)/(l_P\text{-}l_R)$. Approximately the same values are obtained when the progress of reaction is defined alternatively using bond order (n) changes: %Δn$^{\pm}$=100[exp($-l_{TS}/0.6$)-exp($l_R/0.6$)]/[exp($-l_P/0.6$)-exp($-l_R/0.6$)]: (a) G. P. Ford and C. T. Smith, *J. Am. Chem. Soc.* **1987**, *109*, 1325. (b) S. S. Glad and F. Jensen, *J. Chem. Soc., Perkin Trans. 2.* **1994**, 871.

α values may be partly ascribed to the solvent reorganization which lags behind the proton transfer and results in an exalted α value. As in the deprotonations of carbonyl cations, **I** and **II**, the difference in α ($\Delta\alpha = \Delta\alpha_{H_2O} - \alpha_{gas-phase}$) is smaller for α_{SN} (in **V**) than for α_{SO} (in **IV**), most probably due to the weaker solvent reorganization effect expected in water involved in the annihilation of the cationic charge on the pyridinium nitrogen atom in **II** and **V**.

Structural reorganizations measured by the progress of double bond formation in the TS, as defined by %Δl$^{\pm}$=$(l_{TS}-l_R)/(l_P-l_R)\times 100^{(11)}$ where l_{TS}, l_R and l_P are the bond length in the TS, reactant and product, respectively, are ca. 44-47% and 29-30% for S=C (in **IV** for VI_O-like structure) and C=C (pyridine) (In **V** for VI_N-like structure) respectively (Table 3). We note that the progress of structural reorganization is quite similar to the progress of reaction expressed by the experimental α values in water. Thus the experimental α values (α_{SO}=0.45 and α_{SN}=0.29 for CO_3^{2-})[4] can be considered to represent the progress of structural reorganization, implying that the solvent reorganization effect is small, if not absent entirely. This raises us two questions to be addressed: (i) What is then the cause for the difference between the α due to structural reorganization and the gas-phase α obtained theoretically in the present work ($\Delta\alpha_{SO}$= -0.27 and $\Delta\alpha_{SN}$= -0.12 with $\Delta\alpha=\Delta\alpha_{theoretical}$-

$\Delta\alpha_{structural}$)? (ii) Why the two Δα values ($\Delta\alpha_{SO}$ and $\Delta\alpha_{SN}$) differ? The answer to these two questions on the difference in α has been already dealt with in our previous paper[3] on the deprotonations of the ketone series of acids, **I** and **II**. The lower degree of reaction progress based on the theoretical gas-phase α values than the progress of structural changes in the TS is mainly ascribable to the longer distance between the anionic charge center and substituents in the TS (d_{TS}) than in the product anion (d_P), Δd ($=d_P$-d_{TS})<0. The anionic charge center moves to SO_2 moiety (VI_O) and to N on pyridine (VI_N) from the acidic carbon (VI_C) in **IV** and **V**, respectively, on going from the TS to the product anion. The susceptibility of the anionic charge to substituent changes will be smaller in the TS (ρ_{kin}) than in the product (ρ_{eq}) leading to lower values of α ($=\rho_{kin}/\rho_{eq}$), than would be expected for the ideal case at the same distance, Δd=0. This is because a negative Δd leads to a negative Δα, since ρ_{kin} (Δd<0)<ρ_{kin}(Δd=0) and $\Delta\alpha=\alpha(\Delta d$<0)-$\alpha(\Delta d$=0)<0.[3] The exalted α values with positive I ($=\alpha_{CH}$-β_B) observed in deprotonations of many nitroalkanes[2] are exactly the opposite case, *i.e.*, distance between the developing anionic charge center and the substituents in the TS is shorter than in the product anions, Δd>0, in addition to the TS imbalances induced by delayed development of resonance and solvation.

There is the question of the electronic structure of α-sulfonyl carbanions in VI_O. According to the ab initio calculations of the structure of the anion of dimethylsulfone by Bors and Streitwieser,[12] d-$p\pi$-conjugation is not an important factor in stabilizing this anion. This result effectively rules out resonance contributors such as **VII** with significant C=S double-bond character. However in our AM1 results (Table 3), we noted considerable degree (ca. 45%) of C=S double-bond character in the TS. Bors and Streitwieser[12] have suggested that the anionic structure **VII** is stabilized predominantly by either simple Coulombic interactions or by the n-σ^* type sigma conjugative interaction.[13] Indeed if the n-σ^* conjugation prevails, there will be (i) an

VII
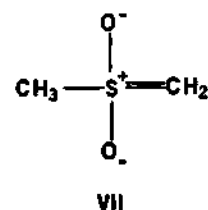
increase in S-C overlap population leading to a double bond character, (ii) an increase in negative charge on the oxygen atom as a result of increased polarization due to populating σ^* orbitals and (iii) a decrease in the S-O overlap population.[13] Since the increased double bond character of the S=C bond is not due to d-$p\pi$-conjugation, there may be no lag in the structural reorganization involving rehybridization from sp^3 to sp^2 to form a partial C=S double bond. This means that ca. 45% structural reorganization found based on the progress of C=S double bond character is a true representation of the progress of reaction in the TS. This is nicely confirmed by determination of the β_B values using substituted anilines as bases in eq. (3), where the proton affinities (PA) are for the substituted aniline bases.[3] The β_B values thus determined were 0.53 for both cations **IV** and **V** (Table 4). Since β_B reflects the progress of deprotonation

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Table 4. Heats of formation (ΔH_f) of the stationary point species, activation parameters ($\Delta H^{\ne}$, $-T\Delta S^{\ne}$, $\Delta G^{\ne}$) and reaction energies (ΔH°, $-T\Delta S^{\circ}$, ΔG°) in kcal mol^{-1} for cation **IV** and **V** with $XC_6H_4NH_2$

| Cation | X | ΔH_f | | | | | Activation Parameters | | | Reaction Energies | | |
		R	RC	TS	PC	P	$\Delta H^{\ne}$	$-T\Delta S^{\ne}$	$\Delta G^{\ne}$	ΔH°	$-T\Delta S^{\circ}$	ΔG°
(Ia)	p-OCH₃	131.6	125.1	131.6	109.8	146.6	0.0	12.1	12.1	15.0	-0.7	14.3
	p-CH₃	161.1	155.0	161.5	140.0	177.5	0.4	12.0	12.4	16.4	-1.0	15.4
	H	168.6	162.8	169.6	148.6	186.6	1.0	12.0	13.0	18.0	-0.7	17.3
	p-CN	198.9	195.4	204.5	185.5	225.1	5.6	12.1	17.7	26.2	-1.0	25.2
	p-NO₂	169.7	160.5	179.2	161.5	203.2	9.5	12.0	21.5	33.5	-0.8	32.7
(IIa)	p-OCH₃	155.7	150.0	156.4	136.5	173.8	0.7	12.2	12.9	18.1	-0.8	17.3
	p-CH₃	185.2	179.5	186.7	166.4	204.8	1.5	12.2	13.7	19.6	-1.3	18.3
	H	192.7	187.3	194.8	175.4	213.9	2.1	12.0	14.1	21.2	-0.9	20.3
	p-CN	223.0	219.3	229.6	211.8	252.4	6.6	12.1	18.7	29.4	-1.3	28.1
	p-NO₂	193.8	186.7	204.2	187.7	230.5	10.4	12.2	22.6	36.7	-1.0	35.7

[a] At 298 K.

by the base, *i.e.*, the progress of C-H bond cleavage, β_B is considered as a better measure of the progress of reaction.[2,4,5] Since β_B indicates *ca.* 53% progress of reaction in the TS, the agreement with the structural reorganization reflected in α_{SO} (=0.45) is somewhat surprising; there is only *ca.* 8% lag in the structural reorganization. Thus the major part, but not all, of the anionic charge on the acidic carbon formed in the TS is transferred almost promptly into the product anion form, VI_O; the TS has *ca.* 45% of the product anion character. Since in the product anion, the anionic charge center on SO_2 moiety is much closer to the substituents Y (in VI_O), Δd is negative ($\Delta d=d_P-d_{TS}<0$) and hence α_{SO} should be depressed, *i.e.*, $\Delta\alpha_{SO}<0$, simply due to this distance factor, $\Delta\alpha_d=\alpha(\Delta d<0)-\alpha(\Delta d=0)<0$. The actual depression of α_{SO} due to the distance factor ($\Delta d<0$) is $\Delta\alpha_d \cong 0.18-0.45=-0.27$.

$$\delta\Delta G^{\ne} = -\beta_B \cdot \delta(PA) \qquad (3)$$

For the cations **V**, the negative charge in the TS (VI_C) shifts to the pyridine nitrogen and annihilate the positive charge on the N atom in the product form, VI_N. Thus here again Δd ($=d_P-d_{TS}<0$) is negative and consequently α_{SN} becomes depressed due to this negative distance factor, $\Delta\alpha_{SN}$ [$=\alpha(\Delta d<0)-\alpha(\Delta d=0)]<0$. In this case, the progress of structural reorganization expressed by the percentage formation of the C=C (pyridine) bond (29-30%) agrees well with the experimental α_{SN} values of 0.29 (for the CO_3^{2-} base). This suggests that the lag due to solvent reorganization is minimal. However our theoretical gas-phase α_{SN} value of 0.17 again reflects the negative distance factor, Δd ($=d_P-d_{TS}<0$), which leads to depression of α ($\Delta\alpha_d=0.17-0.29=-0.12$).

The total negative TS imbalance of $I=\alpha_{SN}-\beta_N=0.17-0.53=-0.36$ comprises (i) the part due to lag in structural reorganization ($I_{str}=0.29-0.53=-0.24$) and (ii) the depression ($\Delta\alpha_d=-0.12$) due to negative distance factor, $\Delta d<0$, *i.e.*, $I=-0.36=\Delta\alpha_d+I_{str}=-0.12+(-0.24)$.

The depression of α due to the negative distance factor, $\Delta d<0$, is greater for α_{SO} ($\Delta\alpha_d=-0.27$) than for α_{SN} ($\Delta\alpha_d=-0.12$), albeit the actual distance change, $\Delta d=d_P-d_{TS}$, involved appears to be greater in VI_N than in VI_O. However, annihilation of (anionic, CH⁻, and cationic, N⁺) charge will certainly reduce the substituent effect and hence the advantage gained by the shorter distance in VI_N compared to

Table 5. Structure-reactivity coefficients for the deprotonations of ketonic (**I** and **II**) and solfonyl carbon acids (**IV** and **V**)

Parameter	Gas-phase(AM1) with NH₃[a]	H₂O[b] (25 °C)
ρ_{kin} (I)	0.82	
ρ_{eq} (I)	4.08	1.38
ρ_{kin} (II)	0.82	
ρ_{eq} (II)	3.77	
α_{CO} (I)	0.20 (0.42-0.44)[f]	0.42[c]
α_{CN} (II)	0.22 (0.46-0.48)[f]	0.26[c]
ρ_{kin} (aniline)	-7.45	
ρ_{eq} (aniline) (I and II)	-12.15	
β_{CO} (aniline)	0.61	0.53-0.55[a]
ρ_{kin} (IV)	0.91	
ρ_{eq} (IV)	4.97	0.47
ρ_{kin} (V)	0.58	
ρ_{eq} (V)	3.43	
α_{SO} (IV)	0.18 (0.44-0.47)[f]	0.45[c]
α_{SN} (V)	0.17 (0.29-0.30)[f]	0.29[c]
ρ_{kin} (aniline)	-4.72	
ρ_{eq} (aniline) (IV and V)	-8.96	
β_{SO} (aniline)	0.53	0.52[a]

[a] Gas-phase AM1 values using NH₃ as a base unless otherwise noted. [b] Experimental values in H₂O at 25 °C.[45] [c] Average values.[4] [d] Determined using various aliphatic primary amine bases.[4,5] [e] For CO_3^{2-} base.[4] [f] Progress of double bond formation in the TS.

that in VI_C. Another factor is that the S atom being a second row element forms a longer (S-CH⁻) bond in the TS so that the shift of the anionic charge center to SO_2 moiety in the product (VI_O) will give a greater decrease in the distance from the substituent. The former reduces the effect of negative Δd in α_{SN}, whereas the latter increases the magnitude of negative Δd in α_{SO}, and in effect $\Delta\alpha_d$ may become greater for α_{SO} than for α_{SN}.

Comparison of the Deprotonations of Ketonic and Sulfonyl Carbon Acids. The relevant Hammett's (ρ) and Brönsted (α and β) for the deprotonations of 4-phenacylpyridinium cation series,[3,5] **I** and **II**, are summarized in Table 5 togather with those obtained in this work for the sulfonyl-activated carbon acids, **IV** and **V**. First of all, in

the deprotonations of ketonic acids, **I** and **II**, sensitibities of substituents to the electron density on the carbanionic carbon atom in **I** and **II** are quite similar both in the TS (**III$_C$**) and in the product (**III$_O$** and **III$_N$**) reflecting nearly even negative charge delocalization to both directions. The structural reorganization involving hybridization changes from sp^3 to sp^2 has progressed to a similar degree as shown by the similar extent of C=C double bond formation in the TS. However this is not true in the deprotonations of sulfonyl acids, **IV** and **V**. The sensitibility of substituents Y to the electron density in **IV** is considerably greater than in **V**, especially in the TS (**VI$_C$**). This is why the experimental as well as theoretical gas-phase α value is greater for α_{SO} than α_{SN}. This large difference in the sensitibility is a correct reflection of the large difference in the progress of structural reorganization as expressed by the degree of double bond formation in the TS, *ca.* 45% of **IV** and *ca.* 29% of **V**. As noted above, in the structure **IV**, n-σ^* type sigma conjugation seems to occur without hybridization changes from sp^3 to sp^2 in contrast to **V** where such rehybridization does occur with the lag of π-delocalization into the pyridinium ring.

The smaller magnitude of ρ values (ρ_{kin} as well as ρ_{eq}) involving substituent (X) changes in the base (aniline) for the sulfonyl carbon acids ($\rho_{kin} \cong -4.7$ and $\rho_{eq} \cong -9.0$) than for ketonic acids ($\rho_{kin} \cong -7.5$ and $\rho_{eq} \cong -12.2$) are due to lower acidity or higher pK_a values of the conjugate bases of the former, sulfonyl acids, **IV** and **V**, relative to the latter ketonic acids, **I** and **II**.[4,5]

In summary, the sulfonyl carbon acids, **IV** and **V**, form somewhat earlier TS than the ketonic carbon acids, **I** and **II**, in the base-catalyzed deprotonation due to the lower acidity. These are reflected in the lower values the Brönsted coefficient α and β for the sulfonyl carbon acids. The major difference between the two systems, however, is that the progress of structural reorganization as expressed by the degree of double bond formation in the TS is similar in the ketone series, **I** and **II**, but is significantly different in the sulfonyl series, **IV** and **V**. The most important factor for this difference is the inability of p-$d\pi$-conjugation involving the sulfur atom in **IV**, where instead n-σ^* type σ-delocalization of the anionic charge takes place without rehybridization (from sp^3 to sp^2), and hence without the lag of π-delocalization. The relatively large negative TS imbalances defined by $I = \alpha_{CH} - \beta_B (<0)$ are mainly the reflection of the longer distance between the anionic charge centers

and substituents in the TS (d_{TS}) than in the product anion (d_P), Δd ($= d_P - d_{TS}$)<0.

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