RATE ENHANCEMENTS DUE TO AQUEOUS SULFURIC ACID IN Mn (III) OXIDATION OF CERTAIN PURINE ALKALOIDS - KINETIC ANALYSIS OF ACIDITY FUNCTIONS

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ABSTRACT

Kinetics and mechanism of purine-based alkaloids like caffeine, theobromine, and theophylline, have been studied using Mn (III) sulfate as an efficient reagent in an aqueous sulfuric acid medium. Progress of the reaction is for the oxidation of xanthine alkaloids has been studied at 520 nm wavelength (λ). Reactions indicated first-order kinetics in [Mn (III)], and [xanthine alkaloid]. Reaction rates accelerated with an increase in acid concentration and temperature. Eyring's and Gibbs- Helmholtz equations were used for the calculation of activation parameters. Observed rate enhancements herein, are analyzed by Zucker-Hammett, Bunnett, and Bunnett-Olsen criteria of acidity functions. The results found as per Bunnett-Olsen criteria of acidity functions, the most plausible mechanism has been proposed by considering the participation of H₂O molecule, as a proton transferring agent in RD (Rate Determining) step.

Keywords: Mn (III) Sulfate Oxidation, Purine-based Alkaloids, Acid Catalysis, Zucker-Hammett, Bunnett, Bunnett-Olsen, Acidity Functions.

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INTRODUCTION

Manganese (Mn) is a versatile d-block element (with the electronic configuration [Ar]4s²3d⁵), which exhibits variable oxidation states from +2 to +7, and the largest being +7. Mn (II) in MnSO₄, Mn (IV) in MnO₂, and Mn (VII) in KMnO₄ are most stable, and these compounds are easily available in any laboratory as desktop chemicals.¹ However, Mn compounds with oxidation states +3, +5, and +6 could also be easily prepared in laboratory.²⁻⁴ A perusal of literature revealed several research studies comprising kinetics and mechanism of oxidation using Mn (III) because it is a strong oxidizing agent in HClO₄ (1.0 M) with a potential $E^{\circ}_{(Mn(III)/Mn(II))} = +1.51$ V. It is known to disproportionate rapidly into Mn (IV), and Mn (II) according to the equilibrium,

It is stabilized by using either excess of Mn (II) or several ligands like sulfate (SO₄²⁻), fluoride (F⁻), pyrophosphate (P₂O₇²⁻), acetate (CH₃COO⁻), and EDTA.⁵⁻⁷ The addition of ligands like pyrophosphate (PyP) reduced the potential from $E^{\circ}_{(Mn(III)/Mn(II))} = +1.51$ V to 1.15V, while EDTA reduced to 0.824 V.^{7,8} The striking importance of Mn (III) as an efficient reagent in electron transfer reactions,⁵⁻¹³ coupled with the biological importance of xanthine alkaloids as Many of these alkaloids find their use as stimulants and vasodilators,¹⁴⁻¹⁶ we have taken up the present kinetic study, involving the Mn (III) sulfate oxidation of purine based alkaloids viz., caffeine (CAF), theophylline (TPL), and theobromine (TBR) in aqueous sulfuric acid (H₂SO₄) solutions. Nevertheless, few publications were found in literature comprising the oxidation of xanthine alkaloids under different conditions.¹⁷⁻²⁰

Scheme-1: Oxidation of Purine Alkaloid to Uric Acid Derivative

EXPERIMENTAL

Materials and Methods

The chemicals (Analytical grade), used in this experimental study, were procured from a local vendor (Avra, SDS, Aldrich, Hyderabad). The HPLC graded Acetonitrile was used and double distilled water used in this study was distilled over alkaline KMnO₄ and acid dichromate in an all-glass apparatus. Purine-based alkaloids like caffeine (CAF), theophylline (THP), and theobromine (THB), were procured from Aldrich, E-Merck or SD fine chemicals. Manganic sulfate (Mn (III)sulfate) was prepared afresh according to the procedure described by Ubbelohde in Vogel's practical book.²¹

Kinetic Method of Following the Reaction

Known amounts of the substrate (Purine alkaloid), sulfuric acid (H₂SO₄), a suitable amount of solvent (water) in one flask; and Mn (III)sulfate in another flask were taken, which were clamped in a thermostatic (constant temperature) bath. After attaining thermal equilibrium, the reaction was commenced when the required amount of Mn (III) was mixed instantaneously and thoroughly to the other contents already taken in the flask. The flask was given a black coating from the outside so that photochemical effects were avoided. Small portions of the reaction mixture were taken, in regular intervals, into a cuvette and absorbance was measured using a thermostatically controlled laboratory visible spectrophotometer. Absorbance (A) or optical density (O.D) values were in agreement with $\pm 3\%$ error.

Reaction Stoichiometry and Products of Oxidation

In a typical experiment, xanthine alkaloid (0.01 mole substrate) and Mn (III)sulfate (0.05 mole reagent) were mixed and made up to 50 mL in an aqueous acidic medium, and allowed to react for about 24 hours at 313K. Aliquots (5.0mL) of the unreacted [Mn (III)] were quenched in known excess of standard Fe (II) solution and titrated with standard Ce (IV) solution using ferroin as an indicator. Obtained results showed that 1.0 (One) mole of xanthine alkaloid utilized 2.0 (Two) moles of Mn (III). In another similar reaction set, after completion, contents of the reaction mixture were extracted using 50 mL of CH₂Cl₂, washed with 40 mL of water. The separated CH₂Cl₂ layer was dried over Magnesium Sulphate, allowed till the solvent got evaporated, and upon purification of the obtained residue by flash column chromatography (SiO₂, ethyl acetate-hexane 1:2) to give uric acid derivatives as the end product, as characterized by NMR and Mass spectroscopic studies. These products are in agreement with the results reported earlier from our laboratory.^{17,18}

1,3,7-Trimethyl Uric Acid (An Oxidation Product of Caffeine)

(m/z) 210; NMR: δ 3.35(N-CH₃); δ 3.41(N-CH₃); δ 3.73(N-CH₃); δ 13.49(O-H)

3,7-Dimethyl Uric Acid (An Oxidation Product of Theobromine)

(m/z) 196; NMR: δ 9.45(N-H); δ 3.24(N-CH₃); δ 3.73(N-CH₃); δ 13.49(O-H)

1,3-Dimethyl Uric Acid (An Oxidation Product of Theophylline)(m/z) 196: NMR: δ 3.35(N-CH₃); δ 3.41(N-CH₃); δ 13.43(O-H); δ 13.92(N-H)**Detection of Free Radicals**

Participation of free radical intermediates in the present study, oxidation of xanthene alkaloids by Mn (III), was supported by free radical-induced vinyl polymerization which afforded a white precipitate and viscous mass (polymer) upon the addition of acryl amide or acrylonitrile to the reaction mixture at elevated temperatures and inert atmosphere while blank experiments by excluding either Mn (III) or xanthene alkaloid did not indicate any sign of polymer formation.

Determination of the Order of Reaction and Salient Kinetic Features

When [Substrate] $\ll$ [Mn (III)], the Plots of [$\ln (A_0/A_t)$] Vs Time were linear with no intercept shows first-order kinetics with respect to [Mn (III)], according to the following first order rate equation:

$$\ln [(A_0)/(A_t)] = (k') t \quad (1)$$

Where A_0 = Absorbance at time of initiating the reaction; A_t = Absorbance at a given time “t”.

Further, (A_0), (A_t) is proportional to the initial concentration of manganic sulfate ($[\text{Mn (III)}]_0$), to the concentration of Mn (III) at a given time “t” ($[\text{Mn (III)}]_t$) respectively. Few representative plots are shown in Fig.-1 to 3. Pseudo-first-order rate constants (k') were obtained from the slopes of these plots, which were determined for all the xanthene alkaloids used in this study at constant acidity, and temperature. Further, the (k') values for the various concentration of substrates were obtained and compiled in Table -1, which indicated constancy in the value of (k') / [Substrate]. This observation suggested that order in [Substrate] is also one.

Fig.-1: Plot of $\ln (A_0/A_t)$ Vs Time for Oxidation Caffeine by Mn (III)
 $10^3[\text{Mn(III)}] = 3.6 \text{ mol/dm}^3$; $10^4 [\text{Caff}] = 3.6 \text{ mol/dm}^3$; $[\text{H}_2\text{SO}_4] = 0.2 \text{ mol/dm}^3$; Temp = 298K

Fig.-2: Plot of $\ln (A_0/A_t)$ Vs Time for Oxidation Theophylline by Mn(III)
 $10^3[\text{Mn(III)}] = 3.6 \text{ mol/dm}^3$; $10^4 [\text{Theophylline}] = 3.6 \text{ mol/dm}^3$; $[\text{H}_2\text{SO}_4] = 0.4 \text{ mol/dm}^3$; Temp = 298K

Table -1: Effect of Variation of [Substrate] on Pseudo First Order Rate Constants(k') at 298 K
 $10^3[\text{Mn(III)}] = 3.6 \text{ mol/dm}^3$; $[\text{H}_2\text{SO}_4] = 0.2 \text{ mol/dm}^3$; Temp = 298 K

$10^4[\text{Substrate}]$ (mol/dm ³)	Pseudo First Order Rate Constant ($10^2 k' / \text{min}$)		
	Caffeine	Theophylline	Theobromine
1.80	1.45	1.59	1.32
3.60	2.89	3.17	2.64
5.40	4.36	4.75	4.02
7.20	5.80	6.38	6.72
9.00	7.30	8.05	7.62

Effect of Variation of Additives on the Rate of Oxidation

Effect of variation of additives like $[\text{Na}_2\text{SO}_4]$, $[\text{H}_2\text{SO}_4]$, and composition of acetonitrile (Vol%) were studied to understand the nature of reaction at 298 K, and the data are compiled in Table-2. Variation of $[\text{Na}_2\text{SO}_4]$ did not affect pseudo first-order rate constant (k') to any notable extent, while an increase in acid concentration increased the rate of oxidation significantly.

Table-2: Effect of Variation of [Additive] on Pseudo First-order Rate Constant (k' / min) at 298 K
 (A) $10^3[\text{Mn(III)}] = 3.6 \text{ mol/dm}^3$; $10^4 [\text{Caff}] = 3.6 \text{ mol/dm}^3$; Temp = 298 K
 (B) $10^3[\text{Mn(III)}] = 3.6 \text{ mol/dm}^3$; $10^4 [\text{Caff}] = 3.6 \text{ mol/dm}^3$; $[\text{H}_2\text{SO}_4] = 0.2 \text{ mol/dm}^3$; Temp = 298 K

Additive	[Additive] (mol/dm ³)	(10 ³ k' / min)		
		Caffeine	Theophylline	Theobromine
(A) H_2SO_4	0.2	28.9	31.7	26.4
	0.4	33.0	34.2	27.8
	0.8	38.3	39.4	33.6
	1.2	43.3	42.5	35.8
	1.6	46.4	45.3	37.8
(B) Na_2SO_4	0.2	28.3	21.9	23.9
	0.4	27.5	20.4	20.3
	0.6	26.2	19.2	20.6
	0.8	28.0	21.0	23.6

RESULTS AND DISCUSSION

Based on their kinetic and spectroscopic results earlier investigators^{5,9-13} suggested that Mn(III) in aqueous sulfuric acid contain different types of species like $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ (or Mn^{3+}), mono hydroxy Mn(III) species ($[\text{Mn}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ or $\text{Mn}(\text{OH})^{2+}$), dihydroxy Mn(III) species ($[\text{Mn}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ or $[\text{Mn}(\text{OH})_2]^+$), and monosulphato Mn(III) species ($[\text{Mn}(\text{SO}_4)]^+$ or $[\text{Mn}(\text{H}_2\text{O})_4(\text{SO}_4)]^+$), disulfato Mn(III) species ($[\text{Mn}(\text{SO}_4)_2]^-$), and trisulfato Mn(III) species ($[\text{Mn}(\text{SO}_4)_3]^{3-}$), according to the following equilibria:

If mono hydroxy or dihydroxy Mn(III) species ($[\text{Mn}(\text{OH})^{2+}]$ or $[\text{Mn}(\text{OH})_2]^+$) is the active species, the rate should have decreased with an increase in the concentration of acid (H_2SO_4) according to the equilibria (4 and 5). On the other hand, if disulfato Mn(III) species ($[\text{Mn}(\text{SO}_4)_2]^-$), or trisulfato Mn(III) species ($[\text{Mn}(\text{SO}_4)_3]^{3-}$) are the reactive species, the addition of sulfate (SO_4^{2-}) should have enhanced the reaction rate according to the equilibria (7,8), followed by retardation in the reaction rate according to the equilibria (9, 10). But, variation of sulfate $[\text{SO}_4^{2-}]$ over a wide concentration range (from 0.001 to 0.01 mol/dm³) did

not alter the reaction rate to any significant extent, ruling out the possibility of either disulfato Mn(III) species ($[\text{Mn}(\text{SO}_4)_2]^-$), or trisulfato Mn(III) species ($[\text{Mn}(\text{SO}_4)_3]^{3-}$) as the reactive species. Based on the foregoing discussions together with the highly significant observed rate enhancements (Table-2) with an increase in acidity, we conclude that monosulphato Mn(III) ($[\text{Mn}(\text{SO}_4)]^+$) species are active species, which is also following equilibrium(6). Thus, a plausible mechanism for the oxidation of caffeine, theophylline, and theobromine comes out as shown in Scheme-2.

Scheme-2: Acid catalyzed Mn(III) Oxidation of Xanthine Alkaloids

Acid Catalysis and Acidity Functions

The dependence of rate constant (k') in dilute acid solutions, when $[\text{acid}] < 0.10 \text{ mol/dm}^3$, is generally interpreted as a function of pH, i.e., $\text{pH} = -\log[\text{H}^+]$. Zucker- Hamett, Bunnett, and Bunnett-Olson ²²⁻³⁴ developed various acidity functions to correlate the dependence of rate constant (k') in highly acidic solutions when $[\text{acid}] \geq 0.100 \text{ mol/dm}^3$. Accordingly, in the present study, the observed rate accelerations (Table-2) in different Bronsted acid concentrations were characterized by the following plots.

Zucker- Hamett plots: $\log k$ vs H_0 ; $\log k$ vs $\log [\text{Acid}]$

Bunnett plots: $\log (k + H_0)$ vs $\log a_w$; $(\log k + \log [\text{acid}])$ vs $\log a_w$

Bunnett-Olson plots: $(\log k + H_0)$ vs $(\log a + \log [\text{H}^+])$; $(\log k + \log [\text{H}^+])$ vs $(\log a + \log [\text{H}^+])$

All the above plots were linear with characteristic slopes and show good to excellent correlation coefficients (R^2) lies in the range of 0.995 to 0.980 (Figs.-3 to 9). Observed slopes of Zucker- Hamett (m and $m^\#$), Bunnett (ω and $\omega^\#$), and Bunnett-Olsen (ϕ , or ϕ^*) plots about this study are presented in Table-3, which were helpful to suggest the participation of water molecule and its significance in the rate-determining step of the mechanism by using the guidelines compiled in Appendix-I.

Table-3: Acidity Function Plots (Xanthine Derivatives) in Different Acid Media

Compound	Theory/Plot	Parameter	H ₂ SO ₄		HClO ₄	
			Slope	R ²	Slope	R ²
Theobromine	Zucker-Hammett- I	m	0.128	0.976	0.311	0.989
	Zucker-Hammett -II	m^*	-0.108	0.983	-0.303	0.947

Theophylline	Bunnett- III	ω	14.2	0.956	7.93	0.959
	Bunnett- IV	ω^*	-12.9	0.913	-10.2	0.940
	Bunnett-Olsen-V	ϕ	-1.11	0.941	-0.701	0.833
	Bunnett-Olsen-VI	ϕ^*	1.21	0.998	1.43	0.998
	Zucker-Hammett- I	m	0.156	0.913	0.243	0.925
	Zucker-Hammett -II	m*	-0.104	0.966	-0.173	0.883
Caffeine	Bunnett- III	ω	16.3	0.994	10.8	0.991
	Bunnett- IV	ω^*	-10.9	0.940	-11.5	0.936
	Bunnett-Olsen-V	ϕ	-1.48	0.965	-1.22	0.925
	Bunnett-Olsen-VI	ϕ^*	1.16	0.998	1.38	0.996
	Zucker-Hammett- I	M	0.220	0.964	0.222	0.980
	Zucker-Hammett -II	m*	-0.187	0.979	-0.220	0.969
	Bunnett- III	ω	12.9	0.974	8.91	0.976
	Bunnett- IV	ω^*	-15.9	0.929	-10.2	0.940
	Bunnett-Olsen-V	ϕ	-0.101	0.938	-0.798	0.870
	Bunnett-Olsen-VI	ϕ^*	1.31	0.997	1.33	0.997

Fig.-3: Plot of $\ln(A_0/A_t)$ Vs Time for Oxidation Theobromine by Mn(III)

$10^3[\text{Mn (III)}] = 3.6 \text{ mol/dm}^3$; $10^4 [\text{Theobromine}] = 3.6 \text{ mol/dm}^3$; $[\text{H}_2\text{SO}_4] = 0.8 \text{ mol/dm}^3$; Temp= 298 K

Data presented in Table-2 reveal that plots (Zucker-Hammett) of $\log k$ vs $[\text{H}_0]$, and $\log k$ vs $\log [\text{Acid}]$ is linear for all the substrates but none of them indicated ideal unit slopes suggesting water molecule participation in the rate-determining step. At the same time, Bunnett's slopes gave unassumingly high slopes. However, Bunnett-Olsen's slopes are somewhat in the range of suggesting H_2O (water) molecule participation either as a nucleophile or as a H^+ (proton) transferring reagent in the rate-determining step, as shown in Scheme-2.

Appendix-I: Summary of Zucker-Hammett, Bunnett and Bunnett-Olsen's Hypothesis

Different Acidity Functions and Kinetic Plots	Slope Value	Function of Water Molecule in the RD Step
Zucker-Hammett (H_0) Plots		
$\log k$ vs H_0	(m) = 1.00	H_2O molecule is not involved
$\log k$ vs $\log [\text{Acid}]$	(m*) $\neq$ 1.00	H_2O molecule may involve
Bunnett Plots	(ω) = -2.5 to 0.0	H_2O not involved
[$\log(k + \text{H}_0)$] vs $\log a_{\text{H}_2\text{O}}$	(ω) = +1.2 to 3.3	H_2O as a nucleophilic agent
	(ω) = +3.3 to 7.0	H_2O as a proton abstracting agent
Bunnett Plots	(ω^*) < (-2)	H_2O as a nucleophilic agent
($\log k - \log [\text{acid}]$) vs $\log a_{\text{H}_2\text{O}}$	(ω^*) > (-2)	H_2O as a proton abstracting agent
Bunnett-Olsen Plots	(ϕ) = -0.34 to 0	H_2O molecule is not involved
(Applicable to weakly basic solutions) ($\log k + \text{H}_0$) vs ($\text{H}_0 + \log [\text{H}^+]$)	(ϕ) = +0.18 to 0.47	H_2O as a nucleophilic agent
	(ϕ) > 0.47	H_2O as a proton transferring agent
Bunnett-Olsen Plots	($\phi^{\#}$) = -0.34 to 0	H_2O molecule is not involved

(applicable to moderately basic solutions) $\log k$ vs $(H_0 + \log [H^+])$	$(\phi^\#) = +0.18$ to 0.47	H ₂ O as a nucleophilic agent
	$(\phi^\#) > 0.47$	H ₂ O as a proton transfer agent

Fig-4: Zucker- Hammett's Plot $\log k'$ vs $\log[H_2SO_4]$
 $10^3[Mn(III)] = 3.6 \text{ mol/dm}^3$; $10^4 [\text{Caff}] = 3.6 \text{ mol/dm}^3$; Temp = 298K

Fig-5: Zucker- Hammett's Plot $\log k'$ vs (H_0)
 $10^3[Mn(III)] = 3.6 \text{ mol/dm}^3$; $10^4 [\text{Caff}] = 3.6 \text{ mol/dm}^3$; Temp = 298K

Fig-6: Bunnett's Plot $\log k'$ vs $(\log a)$
 $10^3[Mn(III)] = 3.6 \text{ mol/dm}^3$; $10^4 [\text{Caff}] = 3.6 \text{ mol/dm}^3$; Temp = 298K

Fig-7: Bunnett's Plot $\log k'$ vs ($\log a$)
 $10^3[\text{Mn(III)}] = 3.6 \text{ mol/dm}^3$; $10^4 [\text{Caff}] = 3.6 \text{ mol/dm}^3$; Temp = 298K

Fig-8: Bunnett- Olson's Plot $\log k'$ vs ($\log a + \log [\text{H}_2\text{SO}_4]$)
 $10^3[\text{Mn(III)}] = 3.6 \text{ mol/dm}^3$; $10^4 [\text{Caff}] = 3.6 \text{ mol/dm}^3$; Temp = 298K

Fig-9: Bunnett- Olson's Plot $\log k'$ vs ($\log a + \log H_0$)
 $10^3[\text{Mn(III)}] = 3.6 \text{ mol/dm}^3$; $10^4 [\text{Caff}] = 3.6 \text{ mol/dm}^3$; Temp = 298K

The rate law for the mechanism at constant acidity comes out as,

$$\frac{-d[\text{Mn(III)}]}{dt} = k[\text{Mn(III)}][\text{Substrate}]$$

(Where *Substrate* = Caffeine, theophylline or theobromine)

The observed kinetics in agreement with the above rate law at any given temperature and acidity. According to Eyring's equation,²²⁻²⁴ $\Delta G^\ddagger$ (free energy of activation) at different temperatures was calculated. The as-obtained ($\Delta G^\ddagger$) values were used to obtain enthalpy ($\Delta H^\ddagger$) and entropy of action ($\Delta S^\ddagger$) from Gibbs-Helmholtz plot (Fig.-10) using Gibbs- Helmholtz equation.²²⁻²⁴

Fig:10- Gibbs-Helmholtz Plot for Oxidation of Caffeine with Mn(III) in H₂SO₄ medium

Effect of Structure on Enthalpy and Entropy Changes

$\Delta S^\ddagger$ (entropy of activation) gives helps to know that whether the reactants are bonded to each other, or not (i.e., molecularity of RD step in a reaction). Negative values and positive values of $\Delta S^\ddagger$ indicate that decrease in entropy is often associated with an associative mechanism and an increase in entropy associated with a dissociative mechanism respectively when a transition state is formed.²²⁻²⁴ An insight into the activation parameters data presented in Table-4 indicated that entropy of activation is negative for Mn (III) oxidation of caffeine, theophylline and theobromine in both sulfuric and perchloric acids. This observation suggests an associative mechanism followed by greater solvation (water molecule participation) in the transition state. On the basis foregoing negative magnitude of entropy of activation, together with the slopes of Bunnett-Olsen's plots, it can be concluded that water participates in the slow step as a proton transfer reagent through hydration in the transition state.

Table -4: Temperature Dependent of Thermodynamic Parameters Mn (III)

Substrate	Temp	(k) (dm ³ /mol/min)	$\Delta G^\ddagger$ (kJ/mol)	GH Eq. $\Delta G^\ddagger = T\Delta S^\ddagger + \Delta H^\ddagger$	$\Delta H^\ddagger$ (kJ/mol)	$-\Delta S^\ddagger$ (J/K/mol)
Caffeine	273	1.75	65.4	$y = 0.2318x + 2.1194$	21.2	232
	283	1.88	67.7			
	293	1.98	70.0			
	298	2.08	71.2			
Theophylline	273	6.75	62.3	$y = 0.2243x + 1.1008$	11.0	224
	283	7.05	64.6			
	293	7.43	66.8			
	298	7.68	67.9			
Theobromine	273	6.30	62.5	$y = 0.2229x + 1.6153$	16.2	223
	283	6.88	64.6			
	293	7.08	66.9			
	298	7.38	68.0			

CONCLUSION

Mn (III) sulfate has been found as an efficient reagent for the oxidation of xanthine alkaloids like caffeine, theophylline, and theobromine in an aqueous sulfuric acid medium. A reaction followed overall second-order kinetics, order concerning [Mn (III)], [xanthine alkaloid] is '1' respectively. Observed rate enhancements herein, are characterized by Zucker-Hammett, Bunnett, and Bunnett-Olsen criteria of acidity

functions. The results of a study of Bunnett-Olsen criteria of acidity functions, the most plausible mechanism has been proposed by considering the participation of water (H_2O) as a proton transferring agent in RD (rate-determining) step. Observed negative values of $\Delta S^\ddagger$ indicated greater solvation in the transition state.

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