



Taft Equation - A Convenient Tool to Decide the Position of Attack in the Reactions of Aliphatic Amines and Thallium(iii)

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ABSTRACT

In our earlier article¹, we had shown the application of Hammett equation of finding the site of attack. The application is based on the relative position of substituent on the aromatic ring from the center of the reaction. We had shown why we have to use σ_m value for σ_p and σ_p value for σ_m value, when we use Hammett's plot. In the present article we have demonstrated the use of the Taft equation for finding the site of attack. Here too, similar necessity arises. Often occasion arises in research, related to oxidation of aliphatic amines, where there is more than one site of attack, and we have to find the right one. One of the sites may be the N-H bond of the functional group; others being the α -C-H bond and the lone pair of electrons of the nitrogen atom. In such a circumstance, the Taft equation plays a deciding role in location of the site of attack. This equation is apparently simple but requires judicious application. It is in the fitness of this aspect, an attempt is made to make the application more understandable and student friendly. Also we feel that it should be essential part of Physical Organic Chemistry Graduate Curriculum.

Keywords: Amines, Oxidation, One Electron Oxidant and Two Electron Oxidant.

INTRODUCTION

The Hammett equation, which is based on the linear free energy relation, does not apply to the reactions of aliphatic compounds and ortho substituted benzene derivatives. This is because of interference of substituent by the reaction center.

Also Hammett's σ values concern groups attached to an aromatic system engaged in resonance.

For aliphatic compounds, the Taft equation in simple form is described as $\log k = \log k_0 + \sigma^* \rho^*$ where k = rate constant for a particular member of a reaction series, k_0 = rate constant for the parent

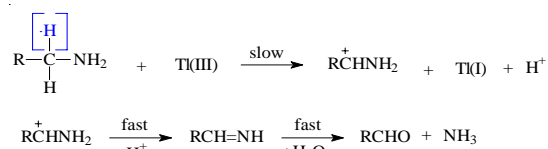
compound, ρ^* = polar reaction constant and σ^* is the polar substituent constant which is the measure of the electron attracting ability of the substituent. It is a purely inductive effect and transmits itself through the aliphatic chain. It is obtained by dividing the total effect of the substituent into steric and polar contributions effect. Taft, further, assumed that the reaction center interacts with substituents, which is the sum of polar effects and steric effects.

If $\log(k/k_0)$ vs σ^* is a straight line (with slope equal to ρ^*), it indicates that the series of the substituted compounds follow the same reaction mechanism. A non-linear plot suggests that the compounds within a series do not adopt the same mechanism. This equation can also be utilized for finding the site of attack in amines. This is discussed in TI(III) oxidations in acetic medium and Cu(III) oxidations in basic medium.

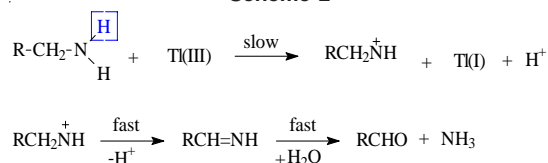
DISCUSSION

A literature survey revealed the work done on the kinetics of oxidation of aliphatic amines is scarce. The oxidation of amines by oxidants like permanganate², lead (IV) acetate³, cobaltic perchloride⁴, N-bromosuccinimide⁵, chlorine dioxide⁶ and TI(III)⁷ have been carried out. TI(III) in acetic acid medium has been used as an oxidizing agent in the oxidation of many organic compounds.

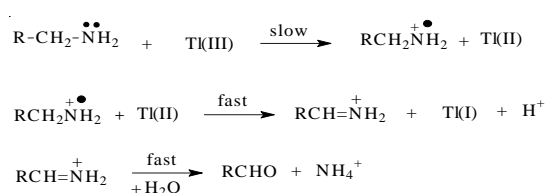
Scheme 1



Scheme 2



Scheme 3



In most cases, TI(III) is converted to TI(I) in a single step. However, oxidations are known where TI(III) is converted to TI(I) in two one electron steps and, therefore, it was thought worthwhile to find the site of attack of the oxidation of amines by TI(III). The first order dependence of the rate, both on TI(III) and amines, and formation of products, NH_3 and RCHO , can be explained by one of the following three schemes.

The three schemes lead to the same products, but differ in the initial attack of TI(III) on the aliphatic amine. In scheme 1 TI(III) attacks RCH_2NH_2 at $\alpha\text{-CH}$, in scheme 2 at NH and in scheme 3 on the lone pair of electrons on nitrogen. Where exactly the attack would take place can be decided by the application of Taft equation? The amines that were oxidized in acid medium were methyl amine, ethyl amine, n-propyl amine, n-butyl amine, iso-butyl amine and n-hexyl amine. If the oxidant attacked at $\alpha\text{-CH}$, the corresponding substituents to the reaction site are shown in Table 1 and each substituent has an σ^* value corresponding to it. Applying the Taft equation for this series of reactions, a plot is constructed, $\log k$ vs σ^* . A straight line with a negative slope was observed, indicating general applicability of the Taft equation. The value of ρ^* , as found from the graph was -5.08 with a good correlation coefficient of 0.9902, indicating the reaction is highly sensitive to the presence of the substituent and the reaction proceeds via an ionic mechanism. Thus, it can be concluded that the amines follow the Taft equation and the site of attack is $\alpha\text{-CH}$ (Table 1, Figure 1).

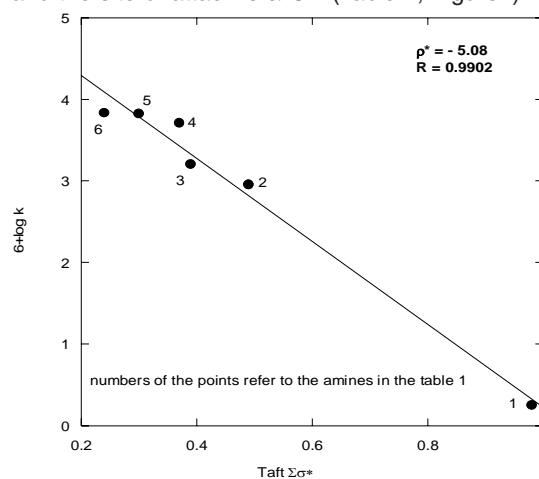


Fig.1. Taft plot for the reactions of amines with TI(III) assuming $\alpha\text{-CH}$ bond breaking

Table. 1: Effect of substituents on k in TI(III) – amine reaction assuming α -CH bond breaking

Sl.No.	Amine	R	Substituents	$\Sigma\sigma^*$	$k \times 10^6 \text{ mol}^{-1}\text{min}^{-1}$	$6 + \log k$
1	methyl	H	H & H	0.98	1.80	0.26
2	ethyl	CH ₃	CH ₃ & H	0.49	900	2.95
3	n-propyl	CH ₃ CH ₂	CH ₃ CH ₂ & H	0.39	1600	3.20
4	n-butyl	CH ₃ CH ₂ CH ₂	CH ₃ CH ₂ CH ₂ & H	0.37	5100	3.71
5	i-butyl	(CH ₃) ₂ CH	(CH ₃) ₂ CH & H	0.30	6640	3.82
6	n-hexyl	n-C ₅ H ₁₁	n-C ₅ H ₁₁ & H	0.24	6800	3.83

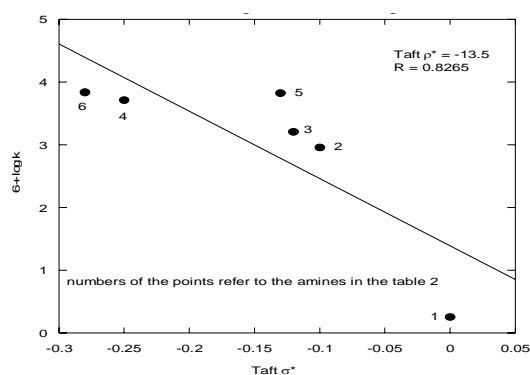
[H₂SO₄] = 1.00 M, [HOAc] = 50% (v/v) m = 1.00 M maintained with KCl, temp. = 318 K

The study of the substituent effect also rules out scheme 2 involving N-H bond rupture. If this were to be the case, then the substituents for the methyl, ethyl, n-propyl, n-butyl, iso-butyl and n-hexyl amines would be themselves methyl, ethyl, n-propyl, n-butyl, iso-butyl and n-hexyl respectively (Table 2). Plot of $\log k$ vs σ^* should be linear. But it was not linear (Fig. 2). When methyl amine is taken as the standard instead of ethyl amine such linearity was not observed supporting scheme 1.

Scheme 3 involves abstraction of an electron from the lone pair of nitrogen, resulting in the formation of the radical cation RCH₂NH₂⁺. Further no polymerization occurred, when acrylonitrile was added. If we assume that if the abstraction of lone pair of electrons on nitrogen occurred then ion with two positive charges on nitrogen would be present. Such a situation is not known. Even if the Taft equation is applied appropriately to scheme 3, again linearity is not observed and the plot would be similar to Fig. 2. Hence the scheme 3 is also ruled out.

The whole yellow highlighted portion is one paragraph. This is very important. Otherwise the whole meaning would change.

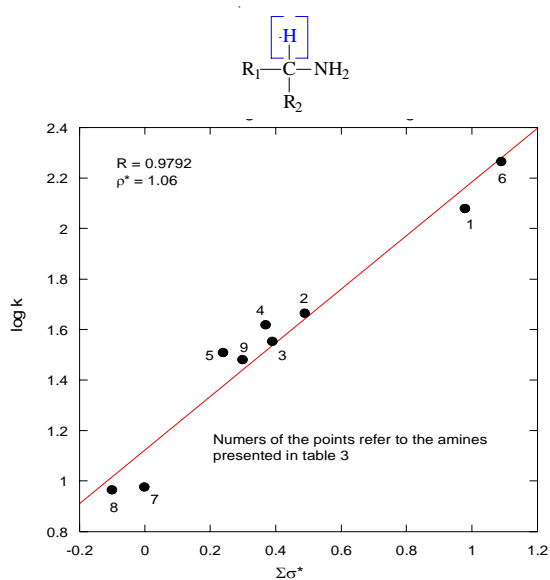
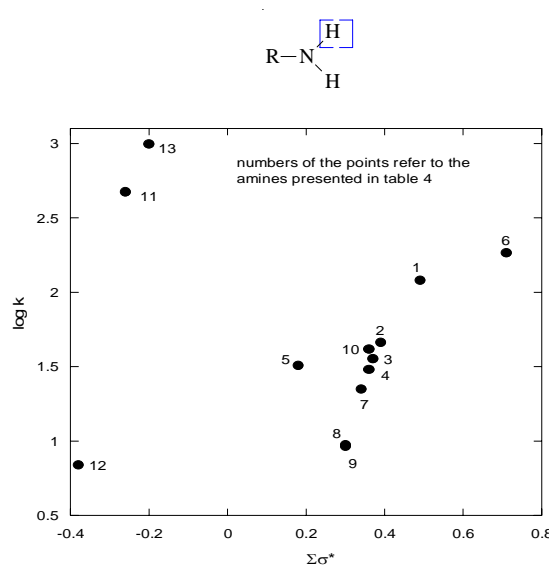
Analogous to the above-mentioned discussion, the site of attack in oxidation of amines by Cu(III) can also be decided using Taft equation.

**Fig. 2. Taft plot for the reactions of amines with TI(III) assuming NH bond breaking****Table. 2 : Effect of substituents on k in TI(III) – amine reaction assuming N-H bond breaking or attack of oxidant on lone pair of electrons of nitrogen. Conditions are same as in Table 1**

Sl.No.	Amine	R	Substituents	σ^*	$k \times 10^6 \text{ mol}^{-1}\text{min}^{-1}$	$6 + \log k$
1	methyl	H	CH ₃	0.00	1.80	0.26
2	ethyl	CH ₃	CH ₃ CH ₂	-0.10	900	2.95
3	n-propyl	CH ₃ CH ₂	CH ₃ CH ₂ CH ₂	-0.12	1600	3.20
4	n-butyl	CH ₃ CH ₂ CH ₂	CH ₃ CH ₂ CH ₂ CH ₂	-0.25	5100	3.71
5	i-butyl	(CH ₃) ₂ CH	(CH ₃) ₂ CHCH ₂	-0.13	6640	3.82
6	n-hexyl	n-C ₅ H ₁₁	n-C ₆ H ₁₃	-0.28	6800	3.83

Table. 3: Effect of substituents on k in Cu(III) - amine reaction assuming α -CH bond breaking

Sl.No.	Amine	R ₁	R ₂	$\Sigma\sigma^*$	k mol ⁻¹ min ⁻¹	log k
1	methyl	H	H	0.98	120	2.079
2	ethyl	CH ₃	H	0.49	46.1	1.664
3	n-propyl	CH ₃ CH ₂	H	0.39	35.7	1.553
4	n-butyl	CH ₃ CH ₂ CH ₂	H	0.37	41.5	1.618
5	n-hexyl	n-pentyl	H	0.24	32.2	1.508
6	benzylamine	C ₆ H ₅	H	1.09	184	2.265
7	i-propyl	CH ₃	CH ₃	0.00	9.46	0.975
8	sec-butyl	CH ₃ CH ₂	CH ₃	-0.10	9.21	0.964
9	i-butyl	i-propyl	H	0.30	30.2	1.480

**Fig. 3 . Taft plot for the reactions of Cu(III) and amines assuming α -CH bond breaking****Fig. 4 . Taft plot for the reactions of Cu(III) and amines assuming N-H bond breaking****Table. 4: Effect of substituents on k in Cu(III) - amine reaction assuming NH bond breaking .**

Sl.No.	Amine	R	$\Sigma\sigma^*$	kmol ⁻¹ min ⁻¹	log k
1	methyl	CH ₃	0.00 + 0.49	120	2.079
2	ethyl	CH ₃ CH ₂	-0.1 + 0.49	46.1	1.664
3	n-propyl	CH ₃ CH ₂ CH ₂	-0.12 + 0.49	35.7	1.553
4	n-butyl	n-C ₄ H ₉	-0.13 + 0.49	41.5	0.976
5	n-hexyl	n-C ₆ H ₁₃	-0.31 + 0.49	32.2	0.964
6	benzylamine	C ₆ H ₅ CH ₂	0.22 + 0.49	184	2.265
7	cy-hexyl	C ₆ H ₁₁	-0.15 + 0.49	22.3	1.348
8	i-propyl	(CH ₃) ₂ CH	-0.19 + 0.49	9.46	0.976
9	sec-butyl	CH ₃ CH ₂ C(CH ₃)H	-0.19 + 0.49	9.21	0.964
10	iso-butyl	(CH ₃) ₂ CHCH ₂	-0.13 + 0.49	30.2	1.480
11	di-n-butyl	(CH ₃ CH ₂ CH ₂ CH ₂) ₂	-0.13 + -0.13	473	2.675
12	di-iso-propyl	[(CH ₃) ₂ CH] ₂	-0.19 + -0.19	6.91	0.840
13	di-ethyl	(CH ₃ CH ₂) ₂	-0.1 + -0.1	990	2.996

Table 5: Effect of substituents on k in Cu(III) - amine reaction assuming attack of the oxidant on lone pair of nitrogen.

Sl.No.	Amine	R	$\Sigma\sigma^*$	$k\text{mol}^{-1}\text{min}^{-1}$	$\log k$
1	methyl	CH_3	$0.00 + 0.49 + 0.49$	120	2.079
2	ethyl	CH_3CH_2	$-0.1 + 0.49 + 0.49$	46.1	1.664
3	n-propyl	$\text{CH}_3\text{CH}_2\text{CH}_2$	$-0.12 + 0.49 + 0.49$	35.7	1.553
4	n-butyl	$n\text{-C}_4\text{H}_9$	$-0.13 + 0.49 + 0.49$	41.5	0.976
5	n-hexyl	$n\text{-C}_6\text{H}_{13}$	$-0.31 + 0.49 + 0.49$	32.2	0.964
6	benzylamine	$\text{C}_6\text{H}_5\text{CH}_2$	$0.22 + 0.49 + 0.49$	184	2.265
7	cy-hexyl	C_6H_{11}	$-0.15 + 0.49 + 0.49$	22.3	1.348
8	i-propyl	$(\text{CH}_3)_2\text{CH}$	$-0.19 + 0.49 + 0.49$	9.46	0.976
9	sec-butyl	$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)\text{H}$	$-0.19 + 0.49 + 0.49$	9.21	0.964
10	iso-butyl	$(\text{CH}_3)_2\text{CHCH}_2$	$-0.13 + 0.49 + 0.49$	30.2	1.480
11	di-n-butyl	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2$	$-0.13 + -0.13 + 0.49$	473	2.675
12	di-iso-propyl	$[(\text{CH}_3)_2\text{CH}]_2$	$-0.19 + -0.19 + 0.49$	6.91	0.840
13	di-ethyl	$(\text{CH}_3\text{CH}_2)_2$	$-0.1 + -0.1 + 0.49$	990	2.996
14	tri-methyl	$(\text{CH}_3)_3$	$0.00 + 0.00 + 0.00$	15.9	1.201
15	tri-ethyl	$(\text{CH}_3\text{CH}_2)_3$	$-0.1 + -0.1 + -0.1$	6.13	0.788

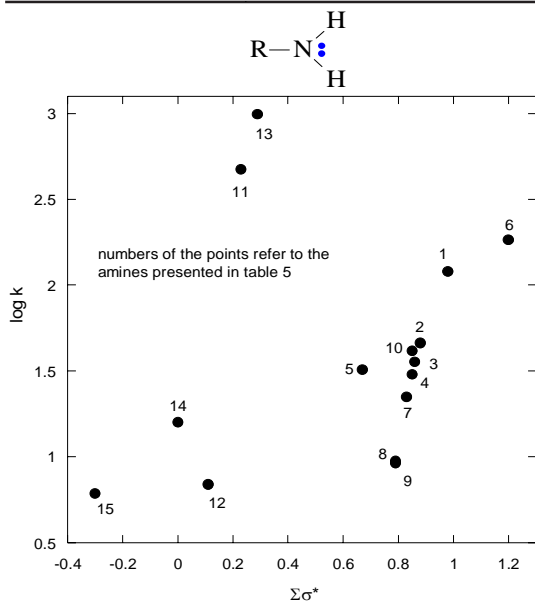
**Fig. 5 . Taft plot for the reactions of Cu(III) and amines assuming nitrogen lone pair attack.**

Table 3, Figure 3 (linearity is observed) and Table 4, Figure 4 (non-linear) and Table 5 (non-linear), Figure 5 are self-explanatory.

It will not be out of place to mention about the application of Taft equation to direct ester oxidation by TI(III)⁸ where polar and steric effects are operative.

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