

## The marvellous Marcus equation

V Jagannadham\*, R. Sanjeev

Department of Chemistry, Osmania University, Hyderabad-500 007, India

Received March 13, 2010; revised November 11, 2010

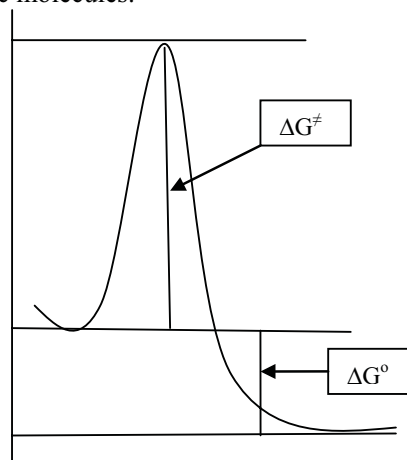
Nitrobenzenes ( $\text{XC}_6\text{H}_4\text{NO}_2$ ) were reduced to their radical anions ( $\text{XC}_6\text{H}_4\text{NO}_2^{\bullet-}$ ) by eighteen different carbon centered radicals derived from formate and simple alcohols, and pyrimidine bases. These radicals were generated by pulse radiolysis in aqueous solution. Carbon dioxide radical anion ( $\text{CO}_2^{\bullet-}$ ) is taken as standard which reacts by direct electron transfer (“non-bonded” or “outer sphere”) with nitrobenzenes. Reaction of  $\alpha$ -hydroxy-iso-propyl radical with nitrobenzenes again proceeds by direct electron transfer (“non-bonded” or “outer sphere”) and some radicals react via addition/electron transfer mechanism (“bonded” or “inner sphere”) giving final products. And the reaction of some radicals stops at the stage of addition to give nitroxide type radicals  $[\text{XC}_6\text{H}_4\text{N}(\text{O}^\bullet)\text{OR}]$  where R is alcohol or pyrimidine moiety on the micro second time scale. The addition/electron transfer mechanisms are well characterized by Marcus theory. All these results are rationalized on the basis of the magnitude of the slopes of Marcus plots established from Marcus theory of one electron transfer mechanisms.

Key words: Marcus Equation, Electron Transfer Reactions.

### INTRODUCTION

The nature of electron transfer reactions in terms of energy considerations is nothing but an amalgamation of activation barrier ( $\Delta G^\ddagger$ ) and thermodynamic driving force ( $\Delta G^\circ$ ). Hence for a thermo neutral reaction ( $\Delta G^\circ = 0$ ) the activation barrier ( $\Delta G^\ddagger$ ) itself is the intrinsic activation barrier ( $\lambda$ ). Marcus equation is a successful treatise for treating kinetic data of electron transfer reactions to separate activation ( $\Delta G^\ddagger$ ) and thermodynamic quantities ( $\Delta G^\circ$ ). Ever since the theory of electron transfer reactions is developed by Marcus [1], interest of kineticists for doing research in this direction has been the central point for understanding the “outer sphere” and “inner sphere” electron transfer reactions. The nomenclature of electron transfer reactions makes frequent use of the terms “outer sphere” and “inner sphere” electron transfer reflects the historical fact that the experimental studies of electron transfer between metal complexes have predominated very often. These terms refer to the structure of the transition states, “outer sphere” denoting that the inner coordination shells of the reacting complexes are left intact in the transition state as to the number and type of ligands originally present, and “inner sphere” meaning that the complexes share at least one ligand of their first coordination spheres in the

transition state. This bridging ligand perhaps provides a continuous pathway of good orbital overlap from metal ion to metal ion. But the notions of “outer sphere” and “inner sphere” mechanisms are not directly applicable to reactions with organic molecules as reacting partners, and hence the terms “non-bonded” and “bonded” have been introduced for electron transfer reactions taking place in organic molecules.



Many articles using the treatment of Marcus theory on several reactions have appeared in literature. These findings include the reactions between several redox pairs of metal ions [2-5], proton transfer at carbon [6-9] and at oxygen or nitrogen [7-10],  $\text{H}^\bullet$  transfer [11],  $\text{H}^\bullet$  transfer [12], nucleophilic addition to carbonyl group [13,14], to carbocations [8, 15], and bimolecular nucleophilic

\* To whom all correspondence should be sent:  
E-mail: jagannadham1950@yahoo.com

aliphatic substitutions [16,17]. In the present article an attempt is made to distinguish between the “non-bonded” single electron transfer reaction from “bonded” single electron transfer reaction using the magnitudes of the slopes of Marcus plots in some free radical reactions where in nitrobenzenes are reduced to their radical anions by a variety of carbon centered radicals generated pulse radiolytically from formate, simple alcohols, and pyrimidine bases. To the author’s knowledge this article may be first of its kind to apply Marcus treatment to electron transfer reactions involving radicals and molecules. The nature of electron transfer in these reactions was published [18, 21] based on the results obtained from ESR and time resolved experiments using pulse radiolysis spectroscopic and conductivity detection systems.

### EXPERIMENTAL

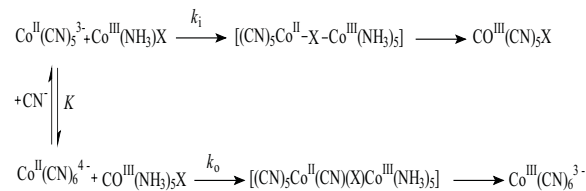
All experimental details and the data used in this article are from the author’s (VJ) work available in literature [18, 21].

### DISCUSSION

Oxidation-reduction reactions involving the transfer of an electron between redox partners have been the subject of many kinetic studies. These redox reactions could be broadly classified in to two categories based on whether the transfer of electron involves ionic sphere or coordination sphere of the redox partners: and the two categories are (a) An outer-sphere electron transfer reaction and (b) An inner-sphere electron transfer reaction. In outer-sphere electron transfer reaction the metal ion retains its full coordination shell and there is a direct electron transfer from the reductant to the oxidant. The electron given by the reducing agent must be transferred from the primary bond system of one complex to that of the other. The essential feature of this mechanism is that there is no transfer of ligands between the reactants. Kinetically the rate of reaction is faster than the rate of substitution of ligands, or the ligand exchange or displacement is slower than electron transfer. And in an inner-sphere electron transfer reaction one of the reactants is labile. In reactions of this class, electron transfers are preceded by the substitution of coordination sphere of one of the ions, with the formation of bridged intermediate in which the two reactants are linked by a common ligand. In this case, ligand displacement is faster than electron transfer process.

These two examples are well explained [4] by a single reaction which involves both the reaction

path ways by an example of oxidation of penta-cyanocobaltate (II) by penta-amminocobalt (III) complexes based on the only results of stoichiometry and kinetics.



When X = PO<sub>4</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>3</sub>, and OAc<sup>-</sup> the reaction followed an outer sphere electron transfer route and when X = Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>, NCS<sup>-</sup> and OH<sup>-</sup> the reaction followed an inner sphere electron transfer route.

We have probed in this article the possibility of using the magnitude of Marcus slopes to distinguish between outer sphere (non-bonded) electron transfer reactions and inner sphere (bonded) electron transfer reactions. A particularly promising opportunity thereby is afforded for the systematic examination of the choice between these two mechanisms.

Successful comparison and properties of electrochemical and chemical rate constants made by Marcus [3] led to arrive at the following equation after rewriting and several rearrangements:

$$\log k = -\log \frac{h}{k_B T} - \frac{\lambda}{4} + \frac{nF}{2 \cdot 2.303 RT} E^\circ \quad (1)$$

Where  $k$  is rate constant,  $h$  Planck constant,  $k_B$  the Boltzmann constant,  $\lambda$  is the intrinsic activation barrier,  $n$  the number electrons transferred from donor to acceptor,  $F$  the Faraday constant,  $R$  the gas constant,  $E^\circ$  is the redox potential or the driving force and  $T$  is temperature in Kelvin scale. And this equation could be obtained as follows from Marcus equation:

According to Marcus [3] for a reaction with weak-overlap electron transfer or non-bonded electron transfer or for an outer sphere electron transfer, the following equation is obtained:

$$\Delta G^\ddagger = \frac{\lambda}{4} + \frac{w_R + w_P}{2} + \frac{\Delta G^\circ}{2} \quad (2)$$

Omitting the work terms [22] ( $w_R$  and  $w_P$  are the quantities of works required to bring the reactants together and for the removal of the products respectively) for proton transfer and electron transfer reactions between molecules or

ions and molecules or radicals and molecules, the final equation obtained was:

$$\Delta G^\ddagger = \frac{\lambda}{4} + \frac{\Delta G^\circ}{2} \quad (3)$$

$\Delta G^\ddagger$  is the free energy of activation and  $\Delta G^\circ$  is the standard free energy change for the process. Therefore for thermo neutral reactions ( $\Delta G^\circ = 0$ )  $\Delta G^\ddagger$  is itself equal to one fourth of the  $\lambda$  which is the intrinsic activation barrier.

From transition state theory provided by Eyring:

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (4)$$

And from electrochemistry for a driving force, the standard free energy change is given by the equation:

$$\Delta G^\circ = -n F E^\circ \quad (5)$$

Taking logarithms of Eq.( 4) and rearranging for  $\Delta G^\ddagger$  we get

$$\Delta G^\ddagger = -2.303 \log \frac{k h}{k_B T} \quad (6)$$

Substituting the values of  $\Delta G^\circ$  and  $\Delta G^\ddagger$  in to Eq. (3) we get

$$-2.303 \log \frac{k h}{k_B T} = \frac{\lambda}{4} - \frac{n F E^\circ}{2} \quad (7)$$

Rearranging the Eq.(7) for  $\log k$  we get

$$\log k = -\log \frac{h}{k_B T} - \frac{\lambda}{4} + \frac{n F}{2 \cdot 2.303 R T} E^\circ \quad (8)$$

Hence for an outer sphere electron transfer (non-bonded) in a given homologous series of reaction, a plot of  $\log k$  versus redox potential ( $E^\circ$ ) should give a straight line with a slope equal to  $\left(\frac{n F}{2 \cdot 2.303 R T}\right)$  and

an intercept equal to  $-\left(\log \frac{h}{k_B T} + \frac{\lambda}{4}\right)$ . Substituting

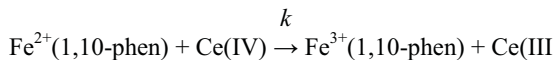
the constants in the quantity for the slope for one electron transfer reaction at 298 K ( $n = 1$ ) yields **8.5 V<sup>-1</sup>**. And from the intercept, again substituting the constants and at 298 K we get

$$\text{Intercept} = 13.21 - \frac{\lambda}{4} \quad (9)$$

$$\text{Or } \lambda = 4 \times (13.21 - \text{Intercept}) \quad (10)$$

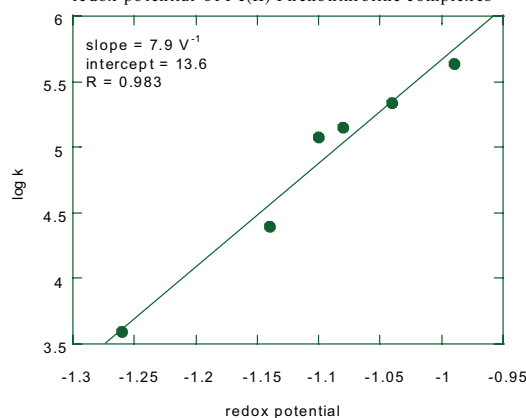
As a specific example, the applicability of Eq.(8) is seen for the oxidation [5] of Fe(II)-tris-

(1,10-phenanthroline) complexes by Ce(IV) in H<sub>2</sub>SO<sub>4</sub> medium at 298 K where in the two redox



partners are inorganic species. A plot of (Fig. 1; R = 0.983)  $\log k$  versus redox potentials of iron complexes was found to be linear with a slope of **7.9 V<sup>-1</sup>** which is very close to **8.5 V<sup>-1</sup>** as predicted by Eq. (8) for an outer sphere electron transfer mechanism. From the intercept the intrinsic activation barrier ( $\lambda$ ) was found to be **-1.4 kJ mole<sup>-1</sup>**. The negative sign of the intrinsic activation barrier is probably an indication of smooth electron transfer from Fe(II) to Ce(IV) with a weak overlap satisfying the so-called Frank-Condon restrictions. And the small magnitude or negligible value of the barrier may be understood that the reaction between Fe(II) and Ce(IV) is an example of a thermo neutral reaction.

Figure 1: Fe(II)(Phe)-Ce(IV) reaction: Plot of  $\log k$  versus redox potential<sup>a</sup> of Fe(II) Phenanthroline complexes



<sup>a</sup> reference 5.

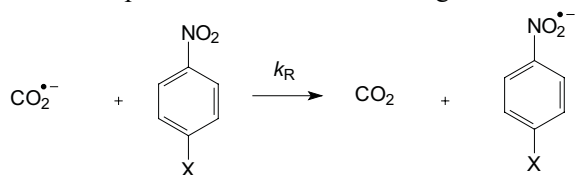
The nature of electron transfer reactions in many organic reactions undergo extensive electronic reorganization and changes in bonding to reacting atoms differ with simple outer-sphere electron transfer reactions for which the Marcus theory was developed to explain. The intrinsic activation barrier for the electron transfer could be taken as a model for the reorganization of the solvent which can assist an optimal tunneling of electron from donor to acceptor.

The main object to discuss the application of Marcus equation to free radical reactions with nitroaromatic compounds is due to the fact that these compounds have widespread potential use in medicine and cancer therapy [23, 24]. There is direct proof that free-radical metabolites are involved in many applications and widespread interest in free-radical intermediates in the action of

several classes of medically important compounds. It is arguable that nitro compounds are the one class of drug in which direct proof of radical production in intact target organisms has been demonstrated [24] and in which the free-radical reaction almost certainly responsible for the therapeutic selectivity has been observed directly [24]. And redox properties control the rate and mode of electron transfer from donors to acceptors. The following are the several examples involving free radical reactions and are classified in to ‘non-bonded’ (outer-sphere) and ‘bonded’ (inner-sphere) electron transfer mechanisms based on the magnitudes of the slopes of Marcus plots. And intrinsic activation barriers ( $\lambda$ ) were also calculated and discussed for all the reactions.

All the radicals were produced pulse radiolytically in  $N_2O$  saturated aqueous solutions containing desired reactants. And these radicals were subjected to react with nitrobenzenes. All the kinetic data used in this article is from the author’s (VJ’s) work [18-21].

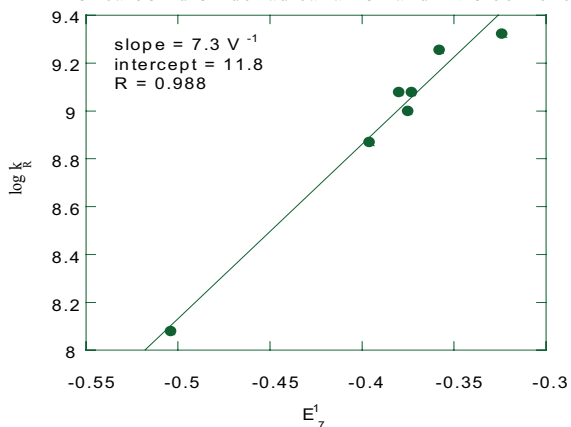
**Carbon dioxide radical anion ( $CO_2^{\bullet-}$ ) [18]:** The Marcus plot for the following reaction:



(rate constant is  $k_R \text{ M}^{-1} \text{ s}^{-1}$ ) was found to be linear (Fig. 2;  $R = 0.988$ ) with a slope of  $7.3 \text{ V}^{-1}$ , the value though not as close as the value of Fe(II)–Ce(IV) reaction to the value of  $8.5 \text{ V}^{-1}$  predicted for an outer-sphere electron transfer reaction, cf. Eq. (8), but it may not be misunderstood that the reaction of carbon dioxide

Figure 2:  $\log k_R$  versus  $E$  for the reaction

of carbon dioxide radical anion and nitro benzenes



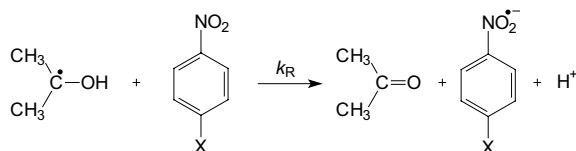
radical anion with nitrobenzenes is not a ‘non-bonded’ (outer-sphere) electron reaction. From the intercept of 11.8 the intrinsic activation barrier ( $\lambda$ ) was found to be  $5.7 \text{ kJ mol}^{-1}$ . The radical anion  $CO_2^{\bullet-}$  was quantitatively oxidized to  $CO_2$  by nitrobenzene and which was confirmed by comparing the yield of  $XC_6H_4NO_2^{\bullet-}$  with that of the quantity obtained by direct reaction of nitrobenzene with hydrated electron [18] ( $e_{aq}^-$ ).

Hence it is concluded that the reaction involves a smooth direct ‘non-bonded’ electron transfer without under going any prime structural changes in the reactants and taken as standard for comparison of the rest of the reactions discussed in this article. The redox potentials of nitrobenzenes used in this figure and in subsequent figures are from reference 24, and for some nitrobenzenes they were calculated using the following equation:

$$E \cong -0.484 + 0.168 \sigma_p^-$$

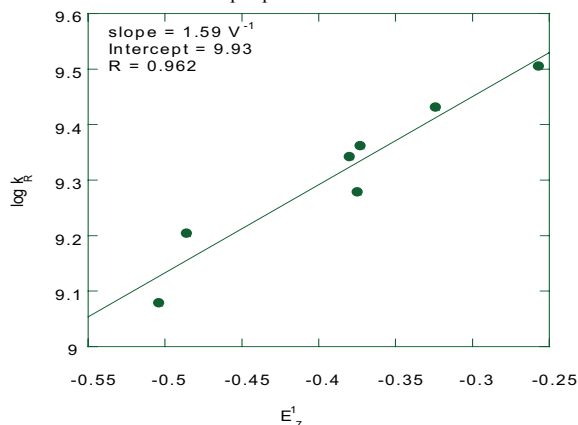
Similar values of redox potentials were reported by S. Steenken [28].

**$\alpha$ -hydroxy-isopropyl radical [ $(CH_3)_2C^*OH$ ] [18]:**

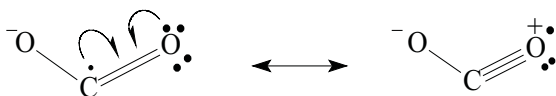


The plot of  $\log k_R$  versus redox potential of nitrobenzenes was linear (Fig. 3;  $R = 0.962$ ) with a slope of  $1.6 \text{ V}^{-1}$  and intercept of 9.9. And this need not be misunderstood that whether the reaction will be proceeding through ‘bonded’ or ‘non-bonded’ electron transfer mechanism since the magnitude of the slope is not on Marcus scale. The  $\alpha$ -hydroxy-isopropyl radical was quantitatively oxidized to acetone by nitrobenzenes and which was confirmed

Figure 3: Plot of  $\log k_R$  versus  $E$  for the reaction of iso-propanol radical with nitrobenzenes.



by comparing the yields of  $\text{XC}_6\text{H}_4\text{NO}_2^-$  with that of the quantity again obtained by direct reaction of nitrobenzene with hydrated electron [18] ( $e_{\text{aq}}^-$ ). And the yields of acetone were checked by GC by comparing with an authentic sample. Hence it is concluded that the reaction again with  $\alpha$ -hydroxy-isopropyl radical involves a smooth direct “non-bonded” electron transfer. In fact the rate constants ( $k_R \text{ M}^{-1} \text{ s}^{-1}$ ) of reaction of all nitrobenzenes studied for the oxidation of this radical was more or less look identical and are close to the rate constant ( $\sim 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) of a diffusion controlled reaction. The rate constants for the reaction of this radical were higher than those observed for the oxidation of carbon dioxide radical anion. Invoking reactivity-selectivity principle here that more reactive radical is less selective and less selective radical is more reactive. And this could be explained due to differences in stabilities of carbon dioxide radical anion ( $\text{CO}_2^{\cdot-}$ ) and  $\alpha$ -hydroxy-isopropyl radical as shown in the following:



This kind of structure for  $\alpha$ -hydroxy-isopropyl radical is not possible hence carbon dioxide radical anion is more stable than  $\alpha$ -hydroxy-isopropyl radical hence more selective.

$\alpha$ -hydroxy-ethyl radical ( $\text{CH}_3\text{CH}^{\cdot}\text{OH}$ ) [18]:

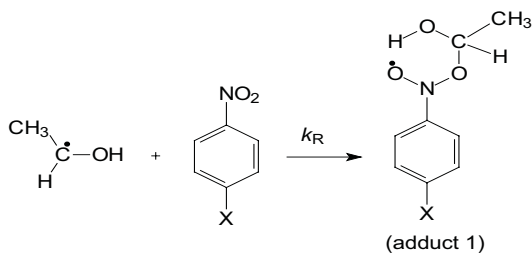
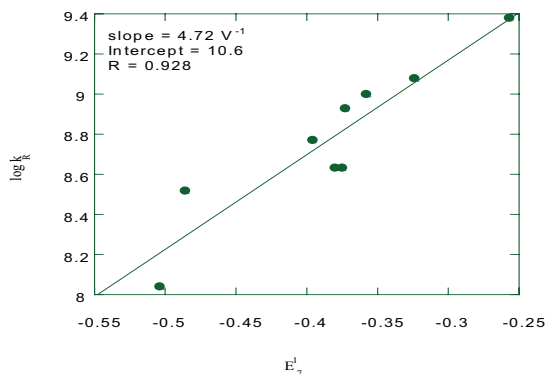


Figure 4: Plot of  $\log k_R$  versus  $E$  for the reaction of ethanol radical with nitrobenzenes



The reaction of this radical with nitrobenzenes underwent in two reaction channels [18]. One involves the formation of nitroxide radical ( $k_R \text{ mol}^{-1} \text{ sec}^{-1}$ ) and the other (see later in the text) giving the radical anion, acetaldehyde and the proton ( $k_s \text{ s}^{-1}$ ). The plot (Fig. 4;  $R = 0.928$ ) of  $\log k_R$  versus redox potentials of nitrobenzenes was fairly linear with a slope of  $4.7 \text{ V}^{-1}$  and with an intercept of 10.6. From the intercept, intrinsic activation barrier ( $\lambda$ ) was found to be **10.4**.

$\alpha$ -hydroxy-methyl radical ( $\text{C}^{\cdot}\text{H}_2\text{OH}$ ) [18]:

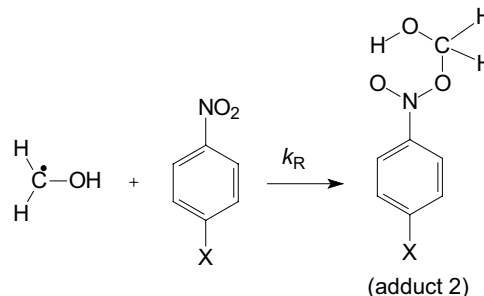
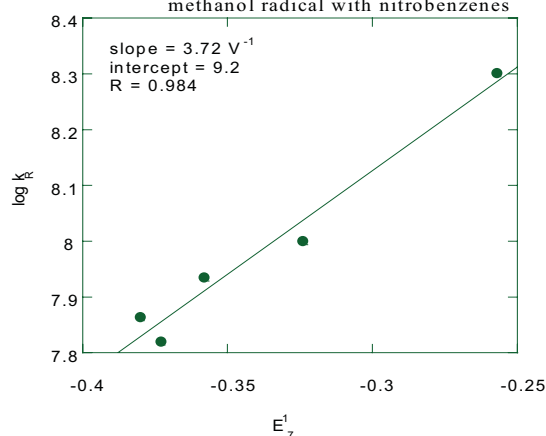


Figure 5: Plot of  $\log k_R$  versus  $E$  for the reaction of methanol radical with nitrobenzenes



The reaction of this radical with nitrobenzenes ended up only with adduct formation unless the pH of the solution raised beyond 7 to give redox products [18]. The plot (Fig. 5;  $R = 0.984$ ) of  $\log k_R$  versus redox potentials of nitrobenzenes was linear with a slope of  $3.72 \text{ V}^{-1}$  and with an intercept of 9.2. The value of intercept leads to 16 as intrinsic activation barrier ( $\lambda$ ). This is again a clear indication that no electron transfer took place.

Reactions of 6-methyluracil-6-yl ( $6\text{-MeU}^{\cdot}$ ), 6-methylcytosine-6-yl ( $6\text{-MeC}^{\cdot}$ ), 6-methyl-dihydrouracil-6-yl ( $6\text{-MeDHU}^{\cdot}$ ) and 2-amino-4,6-dimethyluracil-6-yl ( $2\text{-A-4,6-DMU}^{\cdot}$ ) radicals [20-21]:

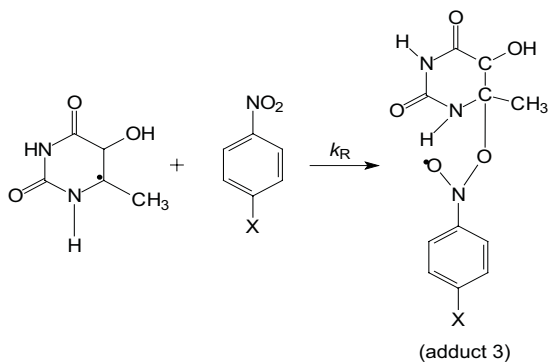


Figure 6: Plot of  $\log k_R$  versus E for the reaction of 6-MeU radical with nitrobenzenes

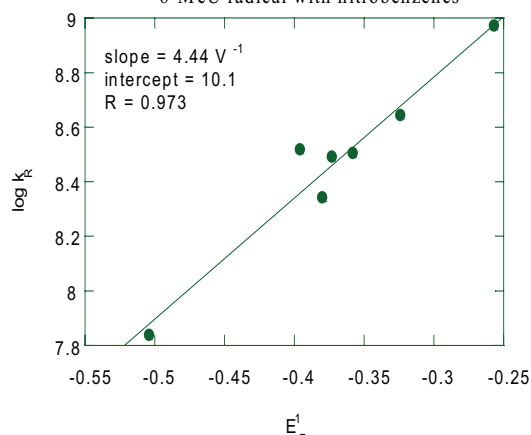
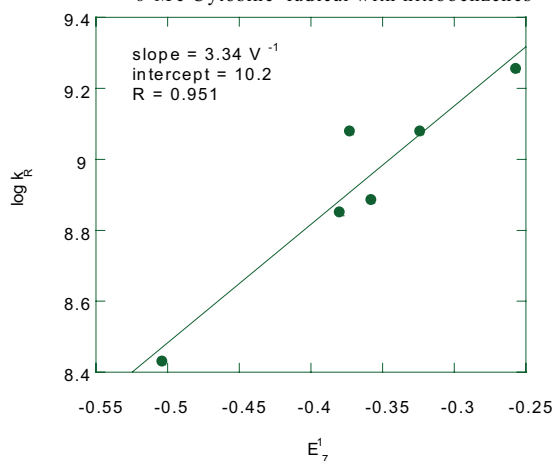


Figure 7: Plot of  $\log k_R$  versus E for the reaction of 6-Me Cytosine radical with nitrobenzenes



The Marcus plots for the reactions ( $k_R \text{ M}^{-1} \text{ sec}^{-1}$ ) of these radicals with nitrobenzenes to give nitroxide type radicals yield the slopes and intercepts **4.44 V<sup>-1</sup>** and 10.1 (6-MeU<sup>\*</sup>: Fig 6, R = 0.973), **3.34 V<sup>-1</sup>** and 10.2 (6-MeC<sup>\*</sup>: Fig 7, R = 0.951), **1.45 V<sup>-1</sup>** and 9.8 (6-MeDHU<sup>\*</sup>: Fig 8, R = 0.914) and **4.95 V<sup>-1</sup>** and 10.6 (2-A-4,6-DMU<sup>\*</sup>: Fig 9, R = 0.999) respectively. The very low values of the Marcus slopes not close to **8.5 V<sup>-1</sup>** are again an indication for the formation of the nitroxide type

adducts only and not for the electron transfer. The intrinsic activation barriers ( $\lambda$ ) were found to be **12.4, 12, 13.6** and **10.4** respectively. Either it is surprise or accident but it is by experimental evidence that the very similar Marcus slopes of the

Figure 8: Plot of  $\log k_R$  versus E for the reaction of 6-Me DHU radical with nitrobenzenes

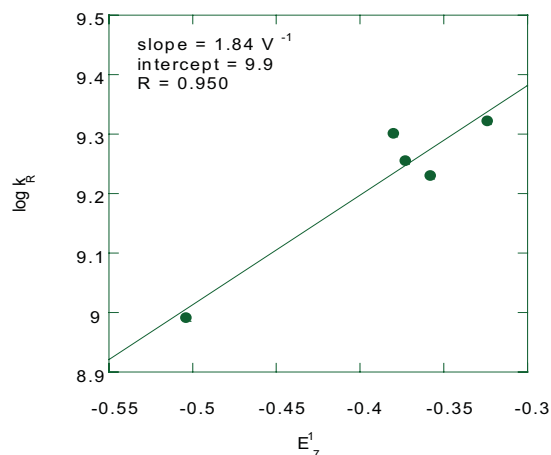
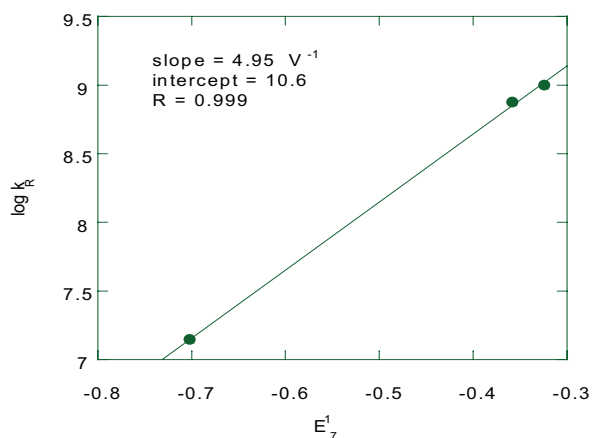
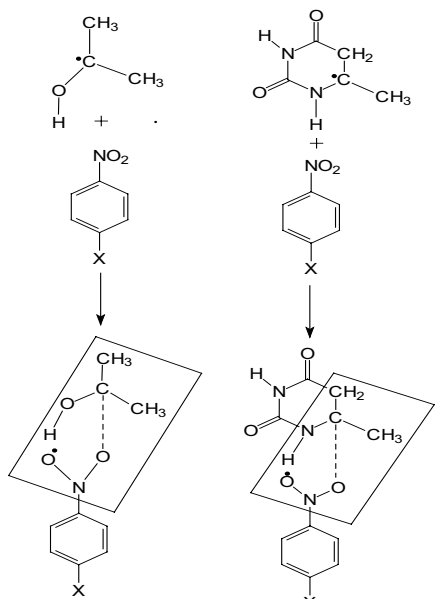


Figure 9: Plot of  $\log k_R$  versus E for for the reaction of 2-A-4,6-DMU Radical



reactions of **isopropyl (1.59 V<sup>-1</sup>)** and **6-MeDHU<sup>\*</sup> (1.45 V<sup>-1</sup>)** radicals shows that the transition states of these two reactions resemble with each other on their way to products in spite of the fact that the two Marcus slopes are one for electron transfer and the other for adduct formation respectively. But before they go to products, the nature of the transition states could be understood as similar ones. This could be seen in the Scheme 1 shown in rectangles [25].

Hence isopropyl radical could be taken as a good model radical for understanding the reduction properties of 6-methyl substituted pyrimidine-6-yl radicals.



Scheme-1

Reactions of uracil-6-yl ( $U^\bullet$ ), cytosine-6-yl ( $Cy^\bullet$ ), and 1-methyl-uracil-6-yl ( $1-MeU^\bullet$ ) radicals [19]

The reactions of these radicals with nitrobenzenes again ended up only with adduct formation unless the pH of the solution raised beyond 7 like in the case of  $\alpha$ -hydroxy-methyl radical ( $\dot{C}H_2OH$ ) to give redox products. The Marcus plots of  $\log k_R$  versus redox potentials of nitrobenzenes were linear with slopes and

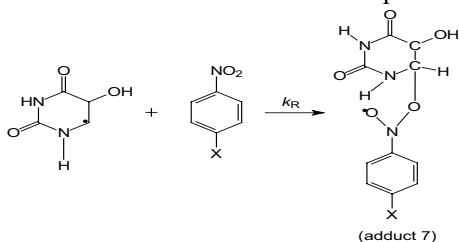


Figure 10: Plot of  $\log k_R$  versus E for the reaction of uracil radical

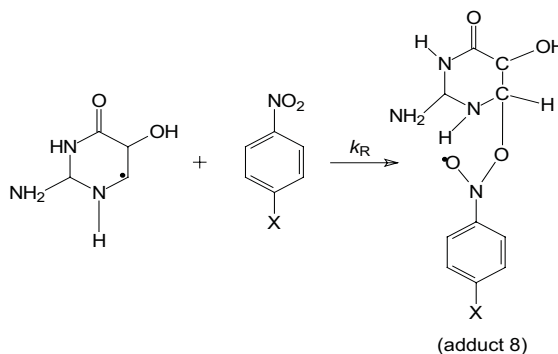
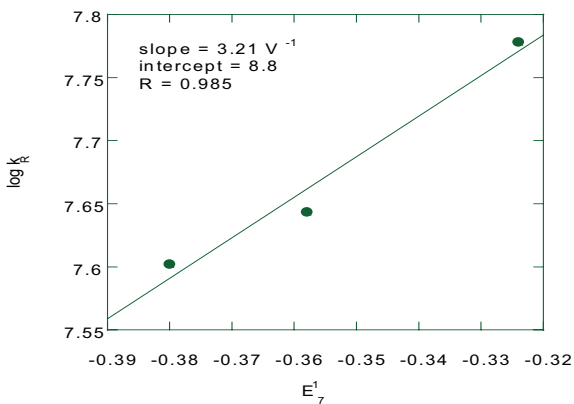


Figure 11: Plot of  $\log k_R$  vs E values for the reaction of Cytosine radical with nitrobenzenes.

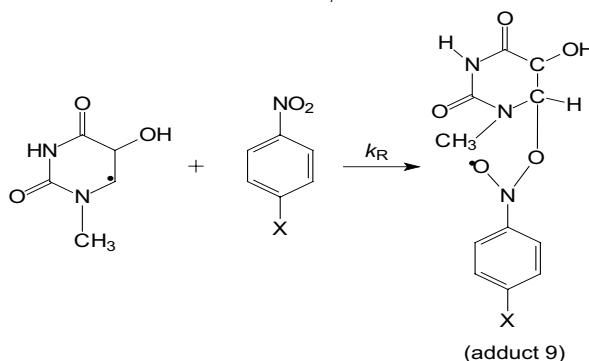
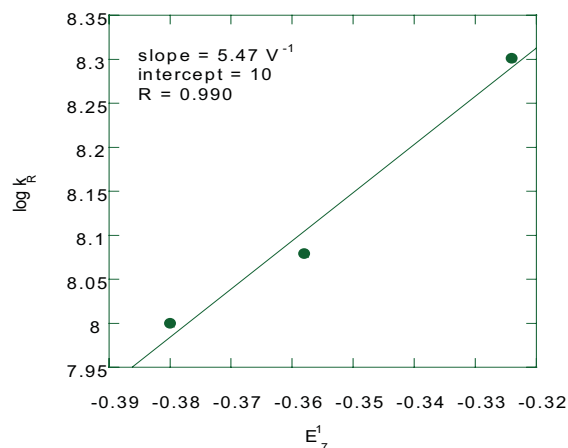
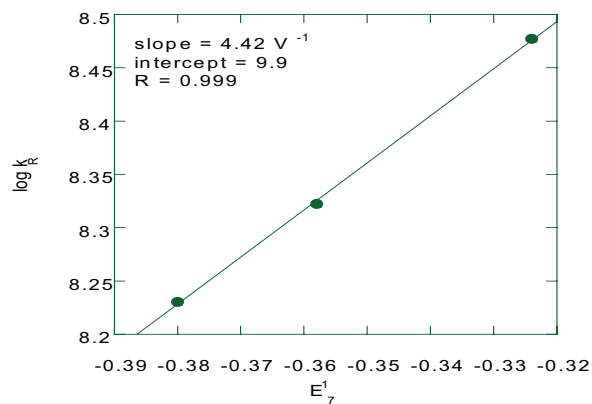
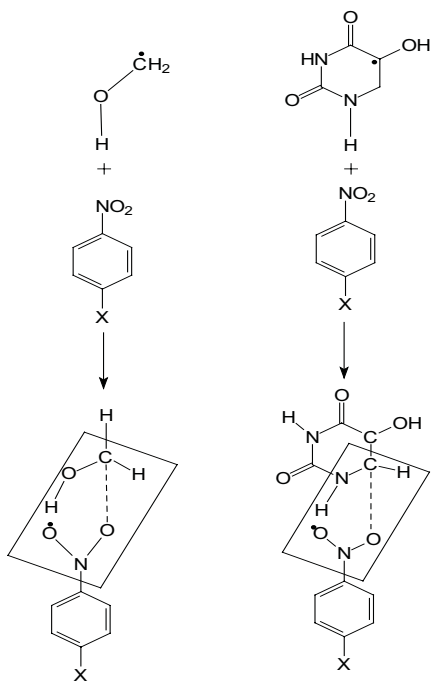


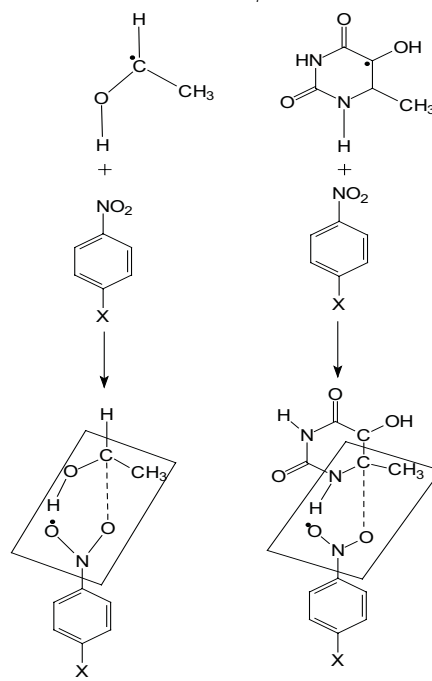
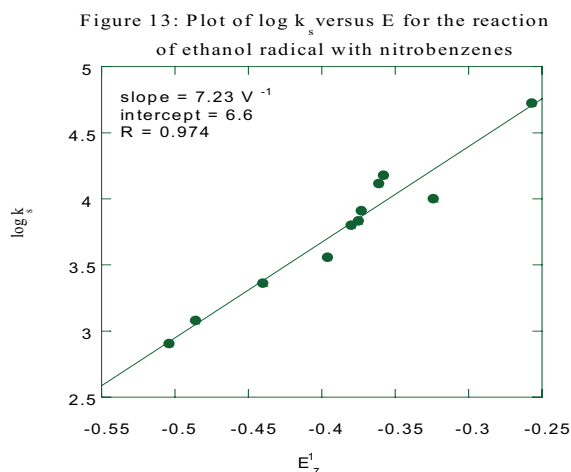
Figure 12: Plot of  $\log k_R$  vs E for the reaction of 1-MeUracil radical with nitrobenzenes



intercepts of  $3.21 \text{ V}^{-1}$  and  $8.8$  ( $\text{U}^\bullet$ : Fig 10,  $R = 0.985$ ),  $5.47 \text{ V}^{-1}$  and  $10$  ( $\text{Cy}^\bullet$ : Fig 11,  $R = 0.993$ ), and  $4.42 \text{ V}^{-1}$ , and  $9.9$  ( $1\text{-MeU}^\bullet$ : Fig 12,  $R = 0.999$ ) respectively. The values of intercepts lead to 17.6, 12.8 and 13.2 as intrinsic activation barriers ( $\lambda$ ). This is again a clear indication that no electron transfer took place between these radicals and nitrobenzenes. And further from similar Marcus slopes of  $3.7 \text{ V}^{-1}$  and  $3.2 \text{ V}^{-1}$  for the reactions of  $^\bullet\text{CH}_2\text{OH}$  and  $\text{U}^\bullet$  radicals respectively, it could be concluded that  **$\alpha$ -hydroxy-methyl radical ( $^\bullet\text{CH}_2\text{OH}$ )** may be understood as a good model radical for **pyrimidine-6-yl ( $\text{U}^\bullet$ )** radicals as shown in Scheme 2.

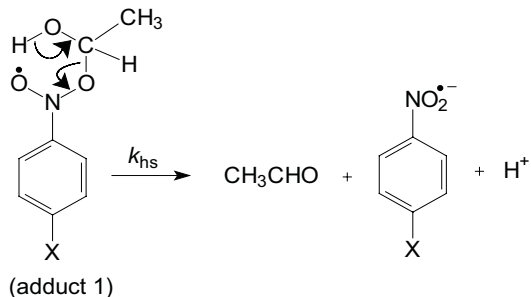


Scheme 2



Scheme 3

The plot of  $\log k_s$  versus redox potentials for the reaction of  **$\alpha$ -hydroxy-ethyl radical** was found to be linear (Fig. 13;  $R = 0.974$ ) with a slope of  $7.2 \text{ V}^{-1}$  and with an intercept of 6.6. From the intercept,



intrinsic activation barrier ( $\lambda$ ) was found to be **26.4**. The very low Marcus slope of  $4.7 \text{ V}^{-1}$  for the first step of the reaction is an indication of adduct formation and not the smooth electron transfer and that of for the second step involving electron transfer is  $7.2 \text{ V}^{-1}$  which is close to the value of  $8.5 \text{ V}^{-1}$  as expected by Eq. (8). Hence the reaction is considered to be an example of addition/electron transfer reaction and from the similar slopes of  $4.7 \text{ V}^{-1}$  and  $4.4 \text{ V}^{-1}$  for the reactions of  $\text{CH}_3\text{C}^\bullet\text{HOH}$  and 6-MeU $^\bullet$  radicals respectively, it could be concluded that  **$\alpha$ -hydroxy-ethyl radical ( $\text{CH}_3\text{C}^\bullet\text{HOH}$ )** may be understood as a good model radical for **6-methyluracil-6-yl (6-MeU $^\bullet$ )** radicals as shown in Scheme 3.



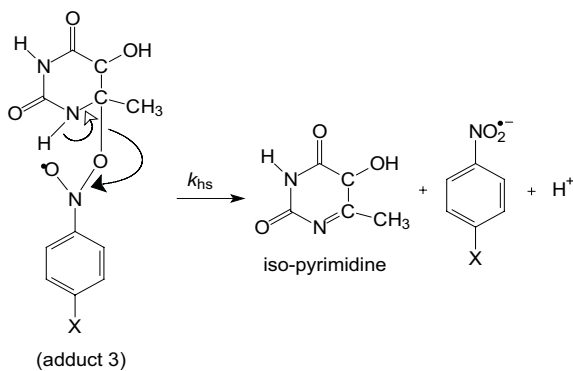


Figure 14: Plot of  $\log k_s$  versus  $E$  for the reaction of 6-Me Uracil radical with nitrobenzenes

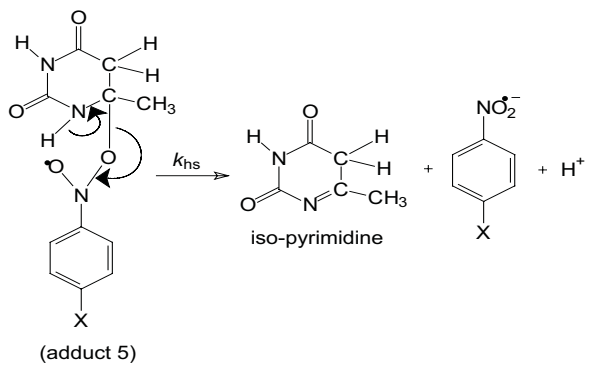
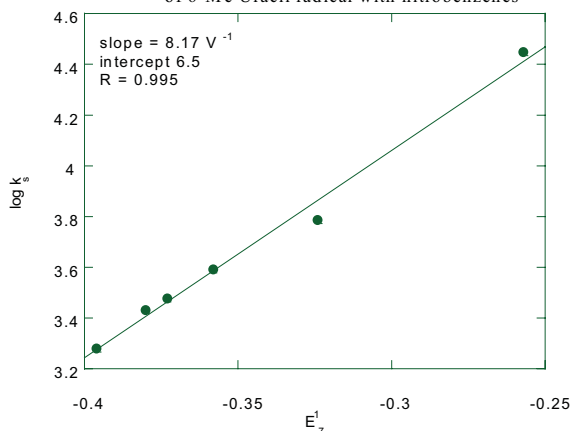


Figure 16: Plot of  $\log k_s$  versus  $E$  for the reaction of 6-Me DHU radical with nitrobenzenes

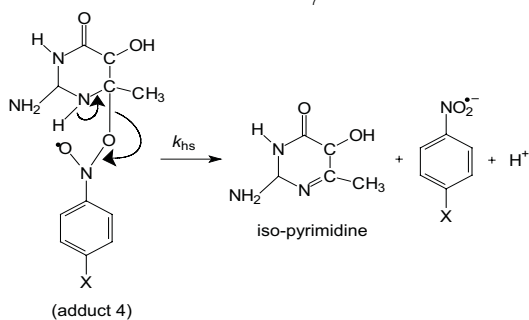
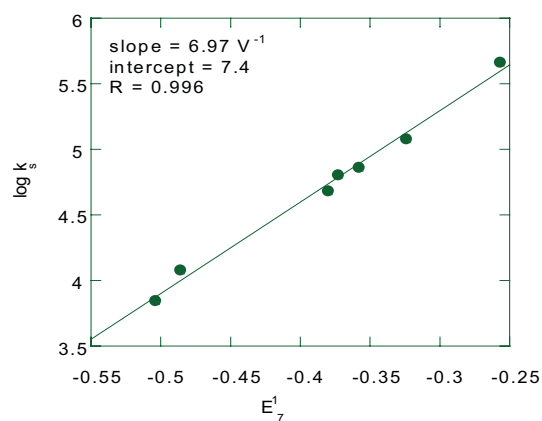


Figure 15: Plot of  $\log k_s$  versus  $E$  for the reaction of 6-Me Cytosine radical with nitrobenzenes

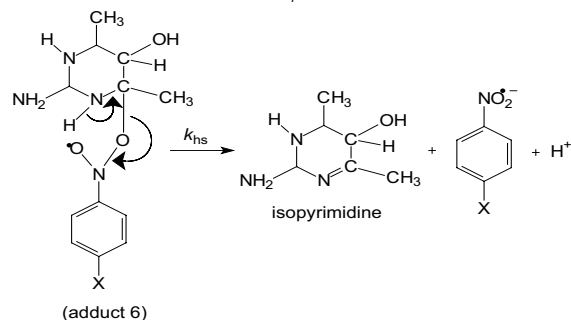
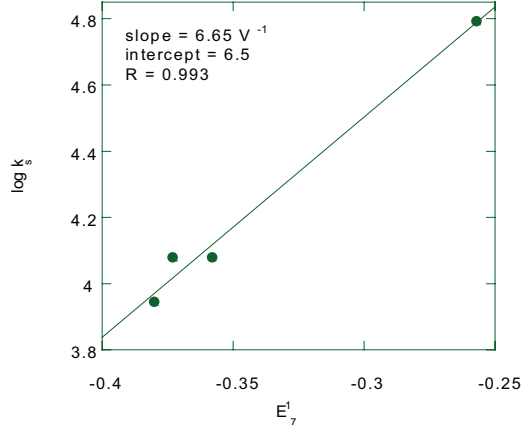
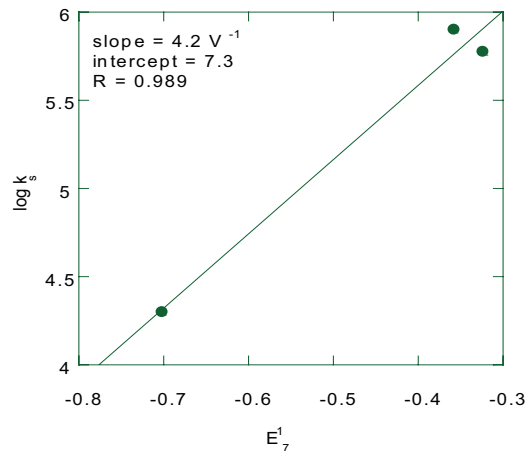
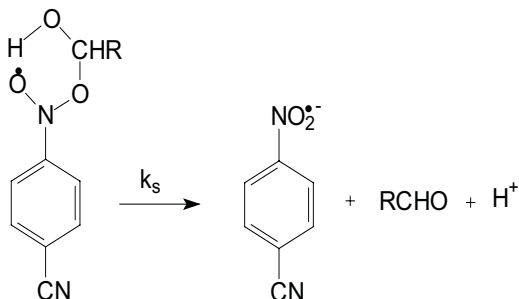


Figure 17: Plot of  $\log k_s$  versus  $E$  for the reaction of 2-A-4,6-DMU radical with nitrobenzenes



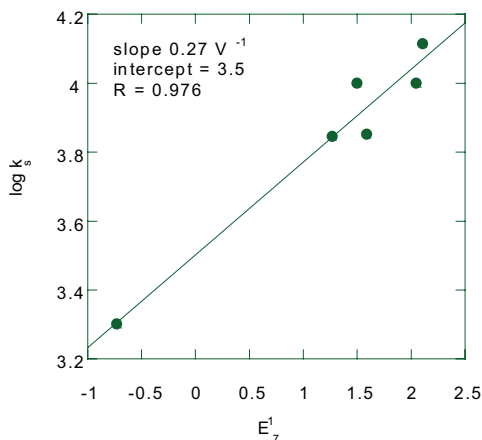
The Marcus plots for the heterolysis reactions ( $k_s$  s<sup>-1</sup>) of the nitroxyl adducts of 6-methyluracil-6-yl (**6-MeU<sup>•</sup>**), 6-methylcytosine-6-yl (**6-MeC<sup>•</sup>**), 6-methyl-di-hydrouracil-6-yl (**6-MeDHU<sup>•</sup>**) and 2-amino-4,6-dimethyluracil-6-yl (**2-A-4,6-DMU<sup>•</sup>**) radicals to give radical anions and other oxidized products yield the slopes and intercepts **8.17 V<sup>-1</sup>** and **6.5** (6-MeU<sup>•</sup>: Fig 14, R = 0.995), **6.65 V<sup>-1</sup>** and **6.5** (6-MeC<sup>•</sup>: Fig 15, R = 0.993), **6.97 V<sup>-1</sup>** and **7.4** (6-MeDHU<sup>•</sup>: Fig 16, R = 0.996) and **4.21 V<sup>-1</sup>** and **7.3** (2-A-4,6-DMU<sup>•</sup>: Fig 17, R = 0.989) respectively. Again the Marcus slopes for the heterolysis reactions are in accordance with electron transfer concept (close to **8.5 V<sup>-1</sup>**).

For the heterolysis step of adducts shown in Figures 13–17 the very similar Marcus slopes (except 2-A-4, 6-DMU<sup>•</sup>) and intrinsic activation barriers (Table 1) it may be further understood that these four adducts undergo heterolysis with similar transition states [25].



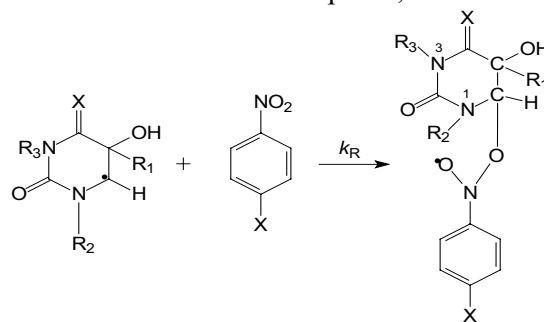
Where R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, n-C<sub>3</sub>H<sub>7</sub>, i-C<sub>3</sub>H<sub>7</sub>, t-Bu, HOCH<sub>2</sub>.

Figure 18: Plot of  $\log k_s$  versus  $E$  for the reaction alcohol radicals with 4-nitrobenzoyl nitrile



Another important and very striking observation is that with a particular given nitrobenzene, in this case with 4-nitrobenzoyl nitrile (4-NBN) the Marcus plot (Fig 18, R = 0.976) for the heterolysis ( $k_s$  s<sup>-1</sup>) of nitroxyl adducts formed with alcohol radicals having a methyl group  $\alpha$ - to

OH and 4-NBN is linear. The redox potentials of various alcohol radicals are from reference 26. But the reason for the very small Marcus slope (**0.27 V<sup>-1</sup>**) in spite of “bonded” electron transfer is not understandable at present. It should have been some where close to **5** or **6 V<sup>-1</sup>**. And from the value of the intercept 3.5, the intrinsic activation barrier ( $\lambda$ ) was found to be 39 kJ mole<sup>-1</sup> which is even more than the values (~23-27) that are observed for the other five adducts. And one more important observation is that with a particular given nitrobenzene, in this case with 4-nitroacetophenone (known as PNAP among radiation chemists) the Marcus plot (Fig 19, R = 0.986) for the formation ( $k_R$  M<sup>-1</sup> sec<sup>-1</sup>) of nitroxyl adducts with various pyrimidine-6-yl radicals is linear with a slope of **1.0 V<sup>-1</sup>**. And from the value of the intercept 7.8, the intrinsic



Uracil: R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = H and X = O

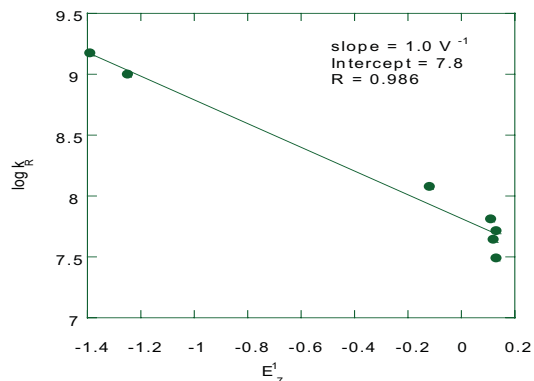
Thymine: R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = R<sub>3</sub> = H and X = O

1-MeUracil: R<sub>1</sub> = R<sub>3</sub> = H, R<sub>2</sub> = CH<sub>3</sub> and X = O

1,3-Di-Me-Uracil = R<sub>1</sub> = H, R<sub>2</sub> = R<sub>3</sub> = CH<sub>3</sub> and X = O

Cytosine: R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = H and X = NH

Fig 19: Plot of  $\log k_R$  versus redox potentials of pyrimidine bases and two alcohols 4-NAP



activation barrier ( $\lambda$ ) was found to be 21.6 kJ mole<sup>-1</sup>. The very small Marcus slope indicates that the reaction is only addition type and not electron transfer. The redox potentials of

Table 1. Summary of the data of Marcus slopes and intrinsic activation barriers.

Radical/reaction	Marcus slope ( $V^{-1}$ )		Intrinsic activation barrier ( $\lambda$ ) kJ mole $^{-1}$	
	For reaction ( $k_R M^{-1} sec^{-1}$ )	For heterolysis ( $k_{hs} sec^{-1}$ )	For reaction ( $k_R M^{-1} sec^{-1}$ )	For heterolysis ( $k_{hs} sec^{-1}$ )
Fe(II)tris-(1,10-phe)- Ce(IV) reaction* This reaction is taken as a reference reaction	7.9 (The expected value is 8.5 based on equation 8, see text)	–	– 1.4	–
CO $_2^{\bullet-}$	7.3	No heterolysis step	5.70	No heterolysis step
(CH $_3$ ) $_2$ C $^{\bullet}$ OH	1.6	No heterolysis step	13.2	No heterolysis step
CH $_3$ C $^{\bullet}$ HOH	4.7	7.2	10.4	26.4
$^{\bullet}$ CH $_2$ OH	3.7	No heterolysis step	16.0	No heterolysis step
6-MeU $^{\bullet}$	4.4	8.2	12.4	26.8
6-MeC $^{\bullet}$	3.3	6.7	12.0	26.8
6-MeDHU $^{\bullet}$	1.5	7.0	13.6	23.2
2-A-4,6-DMU $^{\bullet}$	5.0	4.2	10.4	23.6
U $^{\bullet}$	3.2	No heterolysis step	17.6	No heterolysis step
Cy $^{\bullet}$	5.5	No heterolysis step	12.8	No heterolysis step
1-MeU $^{\bullet}$	4.4	No heterolysis step	13.2	No heterolysis step

\*reference 5.

various pyrimidine-6-yl radicals are from reference 27.

#### CONCLUDING REMARKS

The Marcus treatment (in the form of equation 8) is an excellent tool for identifying the “non-bonded” electron transfer reactions from “bonded” electron transfer reactions taking place in organic molecules.

And it is apparent that a radical with at least one methyl group  $\alpha$ - to OH is essential for a reaction to undergo a “bonded” electron transfer reaction without which no electron transfer is observed. If there are two methyl groups (like the  $\alpha$ -OH-*i*-propyl radical) in the radical  $\alpha$ - to OH, the reaction undergoes exclusively by “non-bonded” electron transfer route and the Marcus slope was not close to **8.5  $V^{-1}$**  as the reactions are close to diffusion controlled limit.

In the case of pyrimidine-6-yl radicals, it is essential that the radical should have a methyl group at 6 position of the pyrimidine for the reaction to go by addition (“bonded”) and then by electron transfer mechanism.

**Acknowledgement:** This article is dedicated to my (VJ's) mentor Prof. Dr. Steen Steenken (Retd), Max-Planck-Institute for Radiation Chemistry, Muelheim a.d. Ruhr, Germany.

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## ЧУДЕСНОТО УРАВНЕНИЕ НА МАРКУС

В. Джаганадхан, Р. Санджиив

*Катедра по химия, Университет Османя, Хайдерабад-500 007, Индия*

Постъпила на 13 март, 2010 г.; преработена на 11 ноември, 2010

(Резюме)

Нитробензени ( $\text{XC}_6\text{H}_4\text{NO}_2$ ) са редуцирани до радикални аниони ( $\text{XC}_6\text{H}_4\text{NO}_2^{\cdot-}$ ) чрез осемнадесет различни въглерод центрирани радикали, получени от формиат и прости алкохоли и пиримидиновите бази. Тези радикали са получени чрез импулсна радиолита във воден разтвор. Радикалният анион на въглеродния диоксид ( $\text{CO}_2^{\cdot-}$ ) се приема като стандарт, който реагира чрез директен електронен пренос ("не-свързан" или "външна сфера") с нитробензени. Реакцията на радикала на  $\alpha$ -хидрокси-изо-пропил с нитробензени също се извършва чрез директен електронен пренос ("не-свързан" или "външна сфера"), а някои радикали реагират чрез механизъм на добавяне/ електронен пренос ("свързан" или "вътрешна сфера") до получаване на крайни продукти. Реакцията на някои радикали спира на етапа на добавяне, за да даде нитроксиден тип радикали [ $\text{XC}_6\text{H}_4\text{N}(\text{O}\cdot)\text{OR}$ ], където R е алкохолна или пиримидинова съставка на микро секундна времева скала. Механизмите на добавяне /електронен пренос са добре описани от теорията на Маркус. Всички тези резултати са рационализирани въз основа на ъгловия коефициент на графиките на Маркус, въведени от теорията на Маркус за механизмите на електронен пренос.