

Permanganate Oxidation mechanisms of Alkylarenes

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Abstract: Permanganate oxidation of benzaldehyde and p-nitrobenzaldehyde goes by two paths, i.e. a major one which is responsible for the normal oxidation giving good second order kinetic and minor path which involves a very small percent of a radical species formed by hydrogen atom abstraction by the permanganate ion. A mechanism involving Hydrogen atom abstraction by permanganate from the alkoxide ion is thus favoured in the permanganate oxidation of p-nitrophenyltrifluoromethylcarbinol. Oxidations of alkylarenes by $n\text{Bu}_4\text{NMnO}_4$ in toluene solvent. Toluene is oxidized to benzoic acid and a small amount of benzaldehyde. The kinetics of the reactions, monitored by UV/vis spectrometry; show that the initial reactions are first order in the concentrations of both $n\text{Bu}_4\text{NMnO}_4$ and substrate. No induction periods are observed. The rate-limiting step in all of the reactions is hydrogen atom transfer from the substrate to a permanganate oxo group. The ability of permanganate to abstract a hydrogen atom is explained on the basis of its ability to form an 80 ± 3 kcal/mol bond to $\text{H}\cdot$, as calculated from a thermo chemical cycle. Rates of $\text{H}\cdot$ abstraction by $n\text{Bu}_4\text{NMnO}_4$ correlate with rates of abstraction by oxygen radicals.

Keywords: Hydride ion transfer, Hydrogen atom transfer, Electron abstraction, Oxygen transfer, Aldehyde ion, trifluoromethylcarbinol

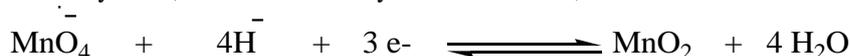
Introduction

The selective oxidation of hydrocarbons is a fundamental transformation in chemistry, important in a wide range of areas from biological to industrial chemistry.[31] The classic examples of stoichiometric hydrocarbon oxidation by metal-oxo species are those of permanganate and chromium(VI) reagents, which have been used for this purpose for over a century.[32] Permanganate has been widely used as a strong, easily handled, readily available, and versatile oxidant, reacting with alcohols, alkenes, aldehydes, saturated C-H bonds, and other function-alities.[7,33,34] The lack of selectivity of permanganate is due, at least in part, to its ability to react readily by either one-electron or two-electron pathways, and its conversion to even stronger oxidants such as " MnO_3^{+} ".[35]

The first example of alkyl arenes with molecular oxygen was published by Ciamician and Silber[1] they allowed toluene, o-xylene, p-xylene, m-xylene for about a year to be influenced by oxygen and Sun light. The corresponding mono carboxylic acid was obtained as main product. IG-Farben produced a method for oxidation of ethyl benzene² The oxidation carried out at 120-130 °C in the presence of Mn-acetate, gave a mixture of acetophenone and phenylmethylcarbinol. KMnO_4 is stable for months in neutral solution, when kept in dark[5] but decomposition is noticeable in acids[6] or in alkaline solution[23] The degradation of organic molecules proceeds via the breakage of covalent bond while manganese undergoes reduction to lower valency state via a number of electron transitions with certain reductants in acidic solution, five electrons change may occur-



In weakly acids, neutral and weakly alkaline solution, there are three electrons change-



And in strong alkaline solution, only one electron change-



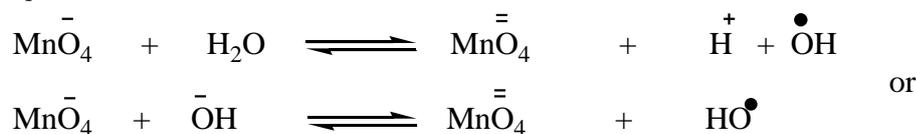
Generally inorganic substance reduces acid permanganate to Mn^{2+} . Whereas organic substance (containing oxidizable hydrogen) stop the reduction at the manganese di-oxide state.

Experimental, results and discussion

Oxy-anion of manganese has importance in many reduction mechanisms. The purple tetrahedral Permanganate ion is known to decompose in alkaline solution according to the equation-



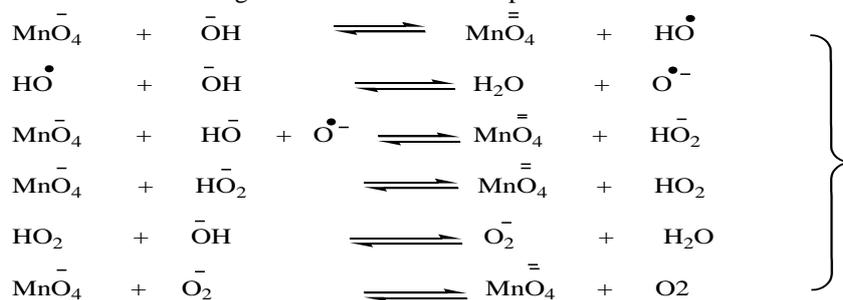
Rate of reaction under various conditions of temperature and concentration of alkali studied by Ferguson and co-workers [23] but they did not produce any mechanism. Later Stamm[7] suggested that the equilibrium



Occur in alkaline solution of potassium Permanganate and this was supported by the fact that in alkaline solution radioactive exchange between the MnO_4^- and MnO_4^{2-} ion is immeasurably rapid and oxidation of a substrate taking place by free hydroxyl radical.

I. MECHANISM ON ALKALINE DECOMPOSITION OF PERMANGANATE

Kinetic studies and mechanism on the alkaline decomposition of permanganate made by Symons⁸ mechanisms involving a series of electron and protons transfer-



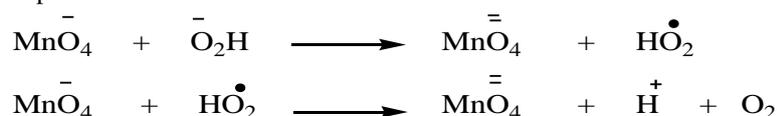
Symons[8] states that the usual mode of oxidation of alkaline permanganate by attack on the substrate by hydroxyl radicals or hydroxyl radical ions. He gives good evidence for this by initiating polymerization of acrylonitrile and styrene in alkaline solution of permanganate. This conclusion is doubted by Drummond and waters[9] Who shown that when diethyl ether, dioxane , t-butanol,propionic, succinic and adipic acids are oxidized by free radicals but not attacked by alkaline permanganate[24] conversely acetone, malonic acid and formic acid are attacked by alkaline permanganate but not by free hydroxyl radical.

II. OXIDIZING POWER OF MANGANATE

Waters and co-workers [9,10] investigated stability and oxidizing power of manganate.[5,34]



Pode and waters[10] postulated a mode of oxidation by strongly alkaline permanganate involving one electron steps.



And each of these oxyanions of manganese can be identified by spectrophotometrically as the reduction takes place. Wiberg and Stewart[11] found that manganate and permanganate oxidized substituted benzaldehyde at the same rate. Since the hydroxyl radical is postulated in the oxidation process. Decomposition by manganous salts is known as Guyards reaction[53] and occurs in neutral and alkaline solution.



The cation Mn^{3+} is involved in the rate determining step of many reactions in the acid solution, but is stable only in concentrated sulphuric acid[38] with fast disproportionation occurring at lower acidities.



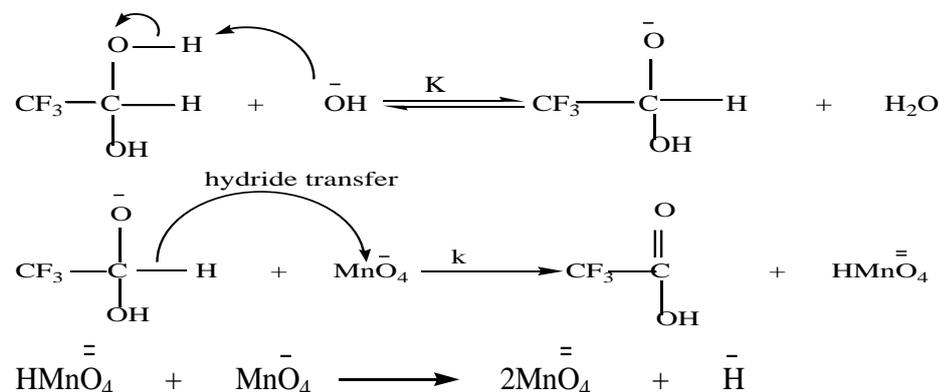
It is possible however to stabilize solutions of Mn^{3+} with complexing agents such as pyrophosphates, which makes them more suitable as oxidizing agents in the pH regions. Waters and co-workers [20,25,26] have extensively investigated that Mn^{3+} oxidation of a number of organic substrates using this technique. Tronov[12] determined rate of reaction between KMnO_4 and a number of alcohol and aldehydes but did not postulate any mechanism. It is found that the oxidation of formaldehyde with permanganate is a base catalyzed.[13]

Drummond and Waters[9] oxidized aldehyde, alcohol, ketones and acids with permanganate and presented a little discussion in term of mechanism.

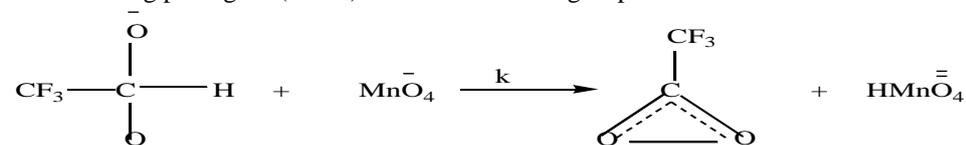
III.SOME MECHANISMS OF PERMANGANATE OXIDATION OF ALKYLARENES

A. Oxidation of 2,2,2-trifluoroethanol

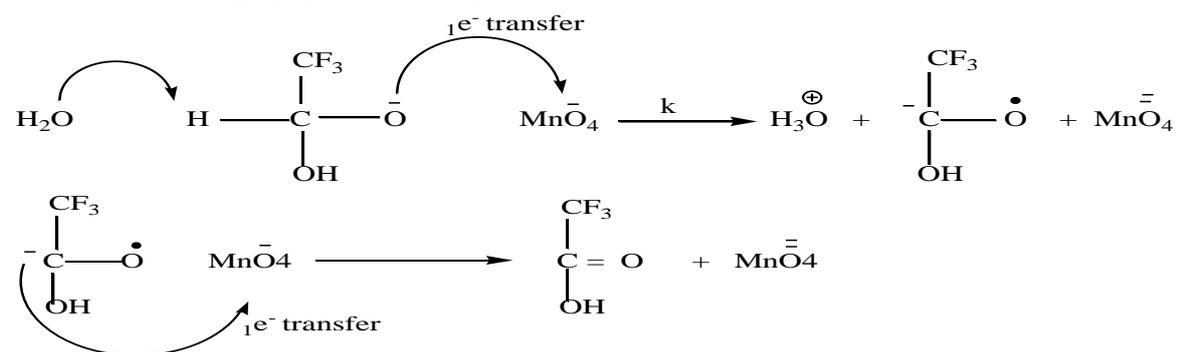
Quantitative conversion of branched chain carboxylic acid to their corresponding hydroxyl acids were found[14] and later co-workers postulated a mechanism involving radical abstraction of a tertiary hydrogen atom by hydroxyl radicals. The oxidation mechanism [4] of alcohol and its deuterium analogue throughout the pH region and compared with 2,2,2-trifluoroethanol and other substituted alcohols which ionize in the pH region, Fluoral hydrate is unique in that it has two acidic hydrogen both can ionize. Deuterium isotope effect were change with nature of substrate, furthermore activation parameters and a positive salt effect show that the transition state in formed from species like charge. These results indicate the hydride ion transfer to the permanganate ion is the rate determining step and mechanism was-



And in strong pH region (12-14) the rate determining step would be -

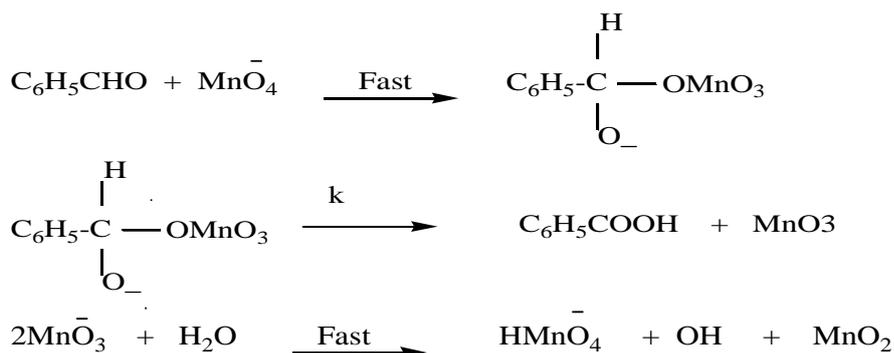


But it was kinetically impossible [55] to distinguish between a mechanism involving the aldehydrol anion as a discreet intermediate and a concerted mechanism involving hydroxyl ion and aldehyde hydrate. Hence termolecular mechanism are also considered-

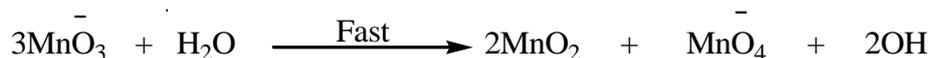
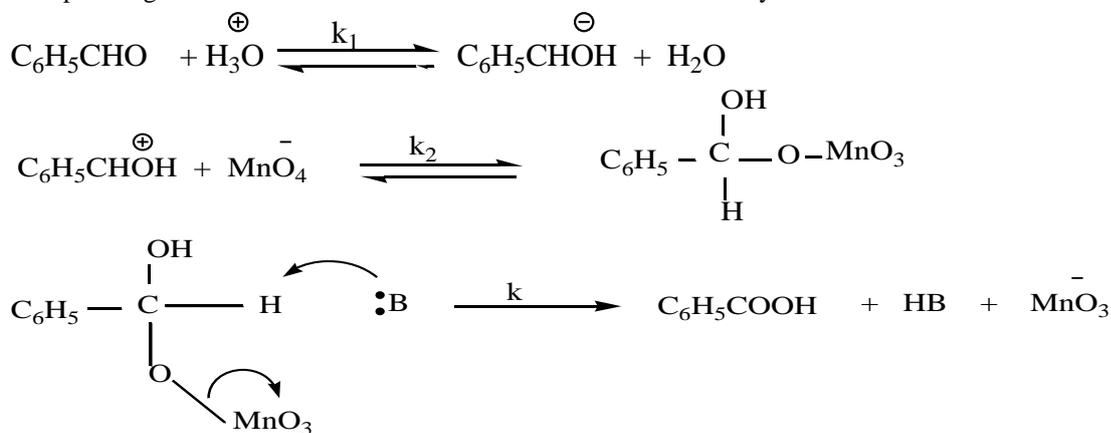


B. Oxidation of benzaldehyde

The permanganate oxidation of benzaldehyde, Tompkins[15] reported a linear increase in rate with hydroxide ion concentration over a very limited range although in basic solution the rate in a given run was found to drop with time and he proposed the following mechanism-

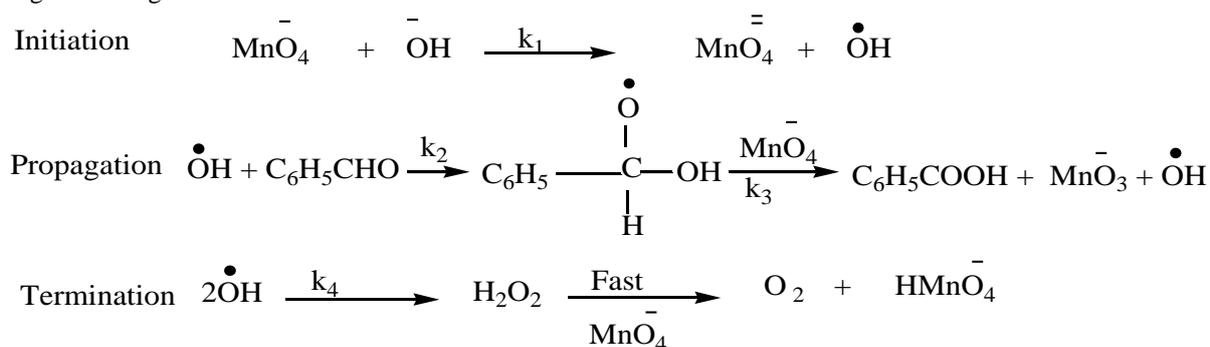


Wiberg and Stewart [11] used deuterium and oxygen-18 labelling technique and found substantial isotope effect in weakly acidic region. This effect decreased with increasing pH as did the oxygen-18 transfer from permanganate to substrate and the reaction found to be acid catalyzed.



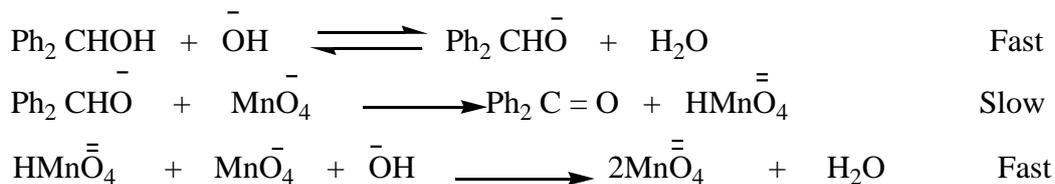
A Hammett plot shown a good linear relation with a negative σ value ($\sigma =$ Hammett substituent constant) one would expect the rate determining step to have a positive σ value, since an electron withdrawing group would facilitate the abstraction of a proton in this step. Equilibrium forming the intermediate ester is proposed having a negative σ value, which is larger in magnitude than that for the rate determining step.

The original proposal of Tompkins [15] was that aldehyde ion could react with permanganate ion by a hydride shift and the effect of substituent on the rate would be in agreement of the stability of the ion. However in order to explain the dependence of the rate on the square root of the hydroxyl concentration then a free radical chain mechanism involving hydroxyl radical was suggested. Furthermore manganate and permanganate were found to react with benzaldehyde with rate of the same order of magnitude. This support a radical mechanism as one would expect a hydride shift to be much slower for magnitude in view of the double negative charge on the ion.



Stewart [17] used deuterium substitution and oxygen-18 exchange shown that the C-H bond is broken in the rate

determining step. The rate showed a dependence on the hydroxyl concentration and positive salt effect. According to this mechanism involving a hydride ion transfer from the benzhydrylate anion to permanganate ion was postulated-

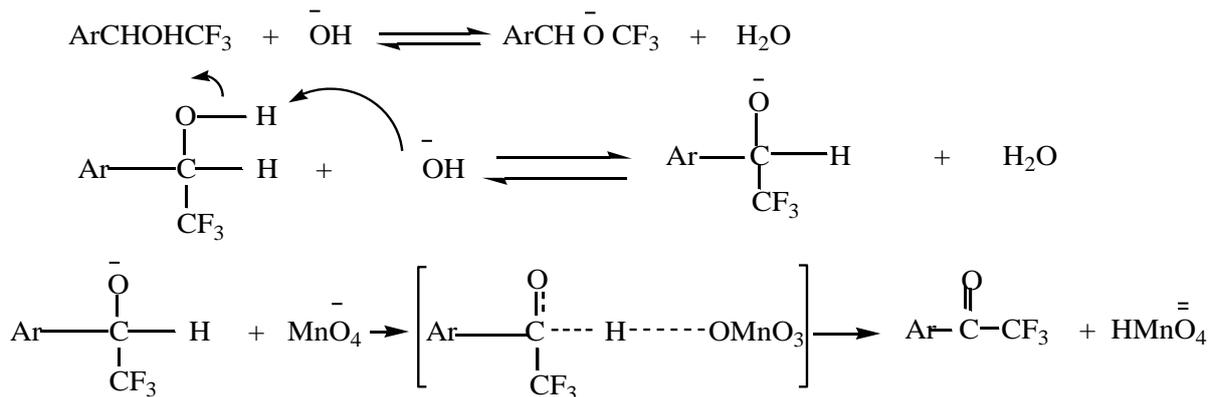


C. Oxidation of Aryl-trifluoromethylcarbinols

Further Aryl Trifluoromethylcarbinols oxidation proved to be satisfactory since they are highly ionized in tenth normal base and oxidized to ketones by KMnO_4 .



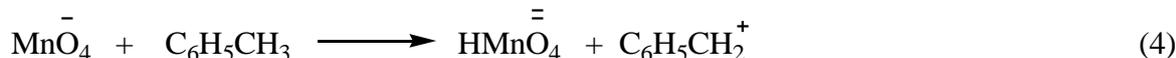
Stewart [17] on the Benzhydrol alcoholate ion is the reactive species if this is so then it should be possible to observe a levelling off of the rate in the region where the alcohol is mostly fully ionized, the rate should be determined by the alcoholate ion present. This has been confirmed.[18,19] Further the observation of positive salt effect, a large negative entropy of activation and a large deuterium isotope effect ($k\text{H}/k\text{D} = 16$) are indicative of a hydride ion transfer mechanism,



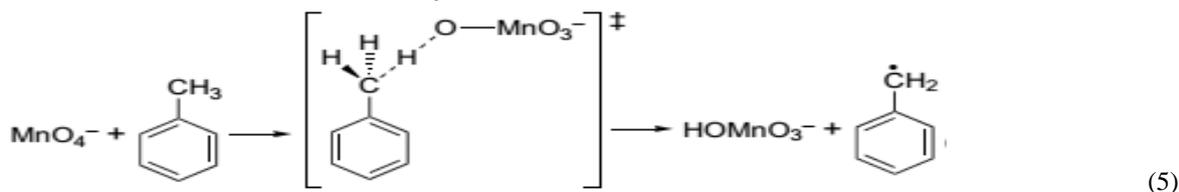
Normal deuterium isotope effects which result from a loss of C-H stretching modes in the transition state are less than half this size at the same temperature.[8] The large effect is observed here is postulated as due to the loss of bending as well as stretching modes in the transition states. The effect of nuclear substitution was found to be slight and this is not in accord with the above mechanism. A hydride transfer from the alkoxide to permanganate should result in a negative σ value. For example a p-methoxy substituent should accelerate and a p-nitro group retard the process. However the reaction rate was found to be only slightly affected by nuclear substitution and further more the small variations in rate which did occur were not related linearly to the Hammett substituent constant (σ).

The following explanations have been presented. Firstly a simple hydride transfer may in fact be occurring with the electronic effect of a distant drop in the molecule being unimportant. Secondly, two different processes with different electronic requirements may be occurring, one with a positive and the other with a negative σ value. Thirdly one of several termolecular mechanisms may be taking place. An example of which is shown below-

precedent, most clearly in the oxidation of alcohols [17] and has been proposed for the oxidation of toluene by MnO_4^- in water [41]. Abstraction of H^- from toluene would form HMnO_4^{2-} and benzyl cation (equation-4), an unlikely process given the observed substituent effects. p-Xylene is only three times more reactive than toluene while it should be much more reactive. p-Chlorotoluene and 4-methylbenzophenone react faster than toluene but should react much more slowly. In addition, the formation of higher-charged species such as benzyl cation is unfavourable in such a nonpolar solution.



Rate-limiting hydrogen atom transfer from the substrate (equation-5) to a permanganate oxo group is consistent with all of the experimental evidence. This is probably the most commonly proposed mechanism for permanganate oxidations of C-H bonds.[11,33,34,48,84] The lack of a solvent effect is characteristic of Radical reactions [49] and is not consistent with polar

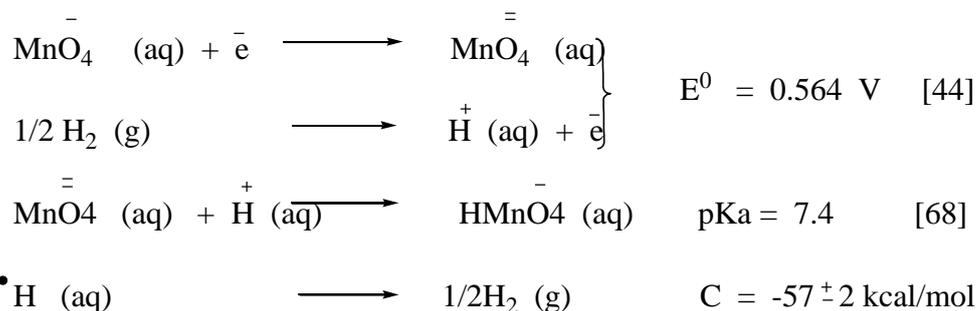


transition states or products. The observed influence of added O_2 is an indicator of radical intermediates (equation-5).

Discussion

Hydrogen atom abstraction reactions exhibit small substituent effects and often do not show a correlation with Hammett σ or σ^+ values. [50, 85] Previous a larger substituent effects are observed because Permanganate is a slower and more selective hydrogen atom abstractor than $\text{tBuOO}\cdot$. The primary isotope effects are consistent with this mechanism, although the measured kH/kD values are not the same as the isotope effects for the $\text{H}\cdot$ transfer step. [29]

Kimberly. A. And co-workers [29] postulated that permanganate and relative oxidants can abstract hydrogen atom ($\text{H}\cdot$) from organic substrate because of the strong bond they form on addition of Hydrogen atom.[56,57,58] Kimberly's [29] data also support this hypothesis. These co-workers [29] perspectives based on enthalpy change contrasts with the standard chemical intuition that a reagent needs to be radical in order to perform hydrogen atom abstraction. This intuition may be reflected in many proposed mechanism of hydrocarbon oxidation, from metalloenzymes to industrial heterogeneous catalysts. [31,59,60,61,67] Permanganate does not fit in this intuition because it is closed shell species. Whose lowest lying triplet state lies roughly 1800 cm^{-1} (51kcal/mol) above the ground state. [62] Since this energy is much larger than the observed energies of activation, a triplet state cannot be a intermediate in the reactions. It should be noted that it is spin allowed for two diamagnetic to react and form a singlet radical pair as in equation-5. Examples of hydrogen atom transfer between closed shell organic molecules have been described by Ruchardt and others [63,64,65] Scheme-1



$$C = \Delta H^0 \left\{ \text{H}\cdot (\text{g}) \longrightarrow 1/2 \text{H}_2 (\text{g}) \right\} - \Delta H^0 \left\{ \text{H}\cdot (\text{g}) \longrightarrow \text{H}\cdot (\text{aq}) \right\} - 1/2 \text{TS}^0 \left\{ \text{H}_2 (\text{g}) \right\} \quad [86]$$

The affinity of MnO_4^- for hydrogen atom is equivalent to its affinity for an electron (its redox potential E^0) and a proton (the acid dissociation constant K_a of HMnO_4^-), following the thermo chemical cycle in the above scheme -1 [$\text{BDE}(\text{H-OMnO}_3^-) = 23.06E^0 + 1.37\text{pK}_a + C$] [69,70] Such cycles have been used by

Bordwell [72,73] and others to determine bond strength to hydrogen in many organic and organometallic compounds [70,71,72,78] above scheme -1 is slightly different from what Kimberly and others used previously [56,57] in part because a recent pulse radiolysis study provided a new value for the pK_a of HMnO_4^- [68,74,75] The constant C is calculated as 57 ± 2 kcal/mol [69,70,71,72,78], with the common assumption that the entropies of MnO_4^- and HMnO_4^- are equal [70,71,72] a value of 80 ± 3 kcal/mol for the H-OMnO₃ bond strength is obtained. Alternatively the constant is not needed if relative bond are calculated from a thermodynamic cycle where hydrogen atom is transferred from another species. HA as in equation-6 (HA = PhOH or PhNH₂). The standard free energy ΔG^0 is calculated in eq-7, from the known E^0 and K_a values [78,79] and is taken to be equal to ΔH^0 because $\Delta S^0 \cong 0$. The derived ΔH^0 is the difference between the H-OMnO₃ and HA bond strength. The solution H-A bond strength are derived from the gas phase value and estimate of differential solvation of HA and A•. Both calculation are in good agreement with $D(\text{H-OMnO}_3^-) = 80 \pm 3$ kcal/mol.[78,79]



$$\Delta H^0 = \text{BDE}(\text{H} - \text{A}) - \text{BDE}(\text{H} - \text{OMnO}_3^-) = 23.06 [E^0(\text{A}^\bullet) - E^0(\text{MnO}_4^-)] + 1.37 [\text{pKa}(\text{HA}) - \text{pKa}(\text{HMnO}_4^-)] \quad (7)$$

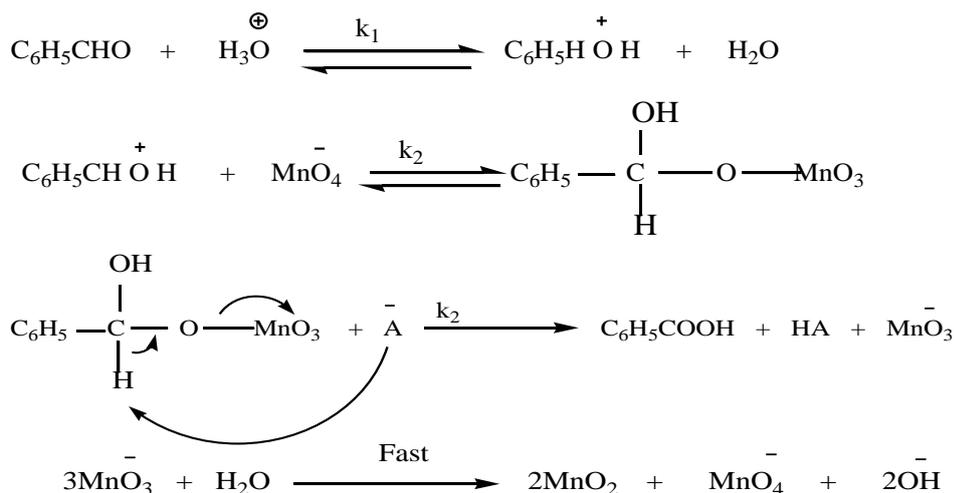
The O-H bond strength of 80 kcal/mol in HMnO_4^- is 9 kcal/mol less than the O-H bond strength in t-BuOOH (89 kcal/mol) [80] and is between the H-Br and H-I bond strengths of 87 and 71 kcal/mol. Since t-BuOO• and Br• readily abstract H• from alkyl aromatic compounds, it is not surprising that permanganate does as well. (Slower rates can be observed for permanganate because it is a stable species, not a fleeting intermediate.) ΔH^0 for the H• transfer steps the difference between the strengths of the bond being broken and that being formed-is a lower bound for ΔH^\ddagger . Therefore, formation of a strong bond to H• is a necessary condition for hydrogen atom abstracting reactivity. The reactions discussed here vary from 9 kcal/mol uphill for H• abstraction from toluene to 6 kcal/mol downhill for abstraction from xanthene (as they observed in their experiment). The data suggest that formation of a strong O-H bond is not only necessary but also a sufficient condition for H• abstraction. It is well established that rates of H• abstraction by main group radical are directly related to bond strengths. OH• reacts with almost organic compounds at close to the diffusion limit,[81] in part because it forms such a strong bond to H• (119 kcal/mol) [80]. tBuOO• is a much less reactive oxidant [82], because it forms a weaker O-H bond of 89 kcal/mol.[80]

Evans and Polanyi suggested in 1936 a linear relationship between activation energies and net enthalpy change in hydrogen atom transfer reactions (equation-8)

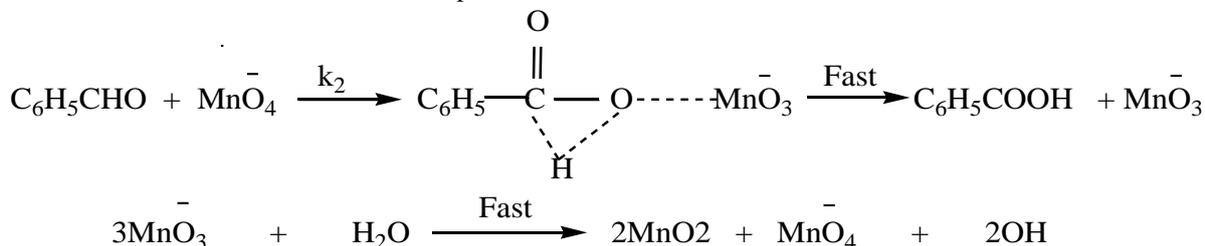
$$E_a = \beta + \alpha(\Delta H) \quad \text{or} \quad \log k \propto \Delta G^\ddagger = \beta + \alpha(\Delta H) \quad (8)$$

and this correlation works quite well over a narrow range of ΔH^0 for similar radicals and substrates. [73,76,77,83] Over a wider range, $\alpha \rightarrow 0$ as the reactions become very exothermic and $\alpha \rightarrow 1$ as the reactions become very endothermic [66]. Kimberly [29] found his data fit the Polanyi eq-8 Well. ΔH^\ddagger and $\log k_2$ for oxidation of the different arylalkanes by n-Bu₄NMnO₄ are proportional to ΔH^0 . The linearity of these relations over the 15kcal/mol range of ΔH^0 is quite good, given the large uncertainties in some of the C-H bond strength. Both $\log k_2$ and ΔH^\ddagger correlate with ΔH^0 because the entropies of activation are essentially constant. These correlations strongly support the assignment of the rate determining step as H• transfer from carbon to an oxo group. The rate of H• transfer from alkyl aromatic compounds to n-Bu₄NMnO₄ also correlate with rate of abstraction by OH•, BuO• and BuOO• [29] and suggested H• transfer terminology.

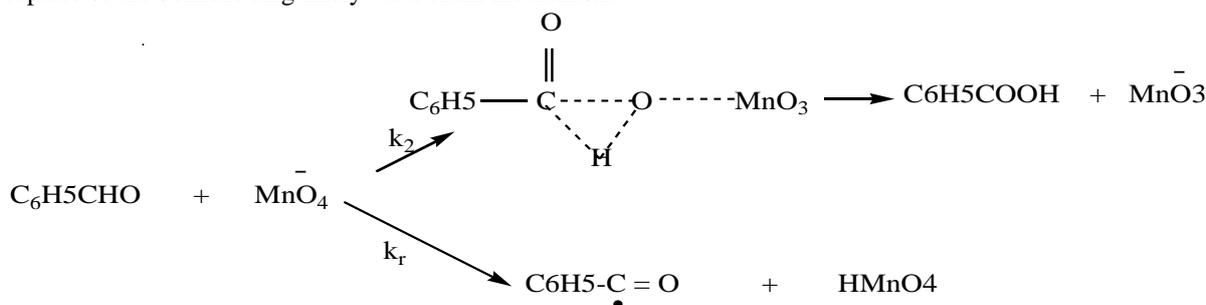
Oxidation of p-Nitrophenylfluoromethylcarbinol with NaOH is a good evidence for abstraction of Hydrogen from alkoxide to permanganate ion. [18] Fleming [52] observed that p-Nitrobenzaldehyde oxidized slower than benzaldehyde and exhibited autocatalysis and both autocatalytic and the initial rates were reduced by a factor of about four fold compared to benzaldehyde at pH 1.40, benzaldehyde $K_2 = 1.64$ (1 mole⁻¹ sec.⁻¹) and p-Nitrobenzaldehyde $K_2 = 0.470$ (1 mole⁻¹ sec.⁻¹). This oxidation shows some dependence on Hydrogen ion concentration. The initial rate of oxidation of p-nitrobenzaldehyde is reduced by almost four fold compared to benzaldehyde at the same pH. This is accord with the negative ρ -value found by Wiberg and co-workers [11] and the mechanism at high pH was proposed.



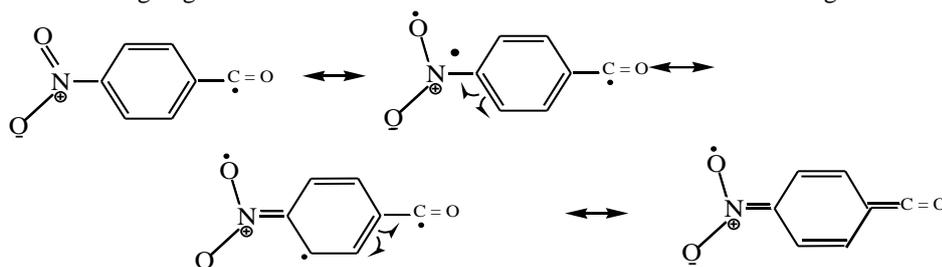
The following mechanism also accommodates the experimental facts found by Wiberg [11] although the ρ - value of the reaction would be difficult to predict.



The autocatalytic effect was found to be reduced by almost four fold for the permanganate oxidation of p-Nitrobenzaldehyde compared to benzaldehyde. For both cases, since experimental evidence shown that the system exhibits overoxidation and it is postulated that the benzene ring is undergoing decomposition at later stage in the reaction. The mechanism is reasonable to suggest a radical reaction path. It seems that permanganate oxidation of benzaldehyde and p-nitrobenzaldehyde goes by two paths, i.e. a major one which is responsible for the normal oxidation giving good second order kinetic and minor path which involves a very small percent of a radical species formed by hydrogen atom abstraction by the permanganate ion. The radical then initiates rapture of the benzene ring likely via a chain mechanism.



The observed reduction of the over oxidation of p-nitrobenzaldehyde is difficult to explain. A similar effect [21] in oxidation of p-nitrotoluene compared to the toluene itself that the electron withdrawing effect of the p-nitro group should retard formation of a radical species does not seem plausible. Perhaps once the radical is formed there is sufficient stabilization due to the p-nitro group to retard the chain reaction which results in ring degradation. Such stabilization would result from the following resonance structures.



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