

# KINETICS AND MECHANISM OF OXIDATION OF PINACOL AND PINACOL HYDRATE BY ALKALINE HEXACYANOFERRATE (III) ION

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The kinetic studies of the oxidation of pinacol and pinacol hydrate has been carried out by hexacyanoferrate (III) in aqueous alkaline medium. The reaction is of the first order with respect to hexacyanoferrate (III). In case of pinacol and pinacol hydrate, the reaction is first order at their lower levels tending towards zero order as the concentration increases. Similarly the first order kinetics was obtained with respect to hydroxide ion at very low concentration and tends to lower order at higher concentrations. The course of the reaction has been considered to proceed through the formation of an activated  $\text{KFe(CN)}_6^{2-}$

diol complex which decomposes slowly into diol radical and  $\text{KFe(CN)}_6^{3-}$  ion.

The radical thus formed is further oxidised to the final oxidation product with more of  $\text{KFe(CN)}_6^{2-}$ . The probable course of the reactions is also described with the help of its oxidation product, oxalic acid.

## INTRODUCTION

Mechanistic studies of reactions in solution have achieved commendable importance during the last few decades. So far as the kinetics of oxidation of these diols are concerned, however, this field has not been studied for several years in alkaline medium. Most of the work in this direction were first carried out using several oxidizing agents, i.e., chromic acid (Heidt *et al.* 1945), vanadium (V), (Littler *et al.* 1960; and Littler & Waters 1960), manganese (III) by pyrophosphate, (Analy *et al.* 1953), periodate (Price & Kroll 1938; Duke & Fernon 1947; and Buist & Bunton 1954), Lead tetraacetate (Crigee 1934; and Bell *et al.* 1958), and cerium (IV) (Richardson 1965) in acidic medium. Recently a good account of their oxidation kinetics was given by Perlin (1969). A limited account of data dealing with the alkaline permanganate (Stewart 1968) oxidation of diols, however, indicates the formation of cyclic ester intermediates. Recently, oxidation kinetics of diols (Singh, V. P. 1973) i.e., ethane 1,2-diol, propane-1, 2-diol and butane-2, 3-diol, in aqueous alkaline medium have been studied with hexacyanoferrate (III) in presence of osmium tetroxide as a homogeneous catalyst. For further information concerning the uncatalysed oxidation kinetics of diols in aqueous alkaline medium, the authors now wish to report our result on the kinetics of oxidation of pinacol and pinacol hydrate with hexacyanoferrate (III).

## MATERIALS AND METHODS

The samples of Pinacol and Pinacol hydrate used in this investigation were of analytical grade. Potassium ferricyanide, Potassium chloride and the sodium hydroxide used were of GR (S. Merck) grade.

Kinetic measurement were made as described elsewhere (Singh & Nath 1962;

and Singh, H. S. 1963). Their standard solutions were always prepared in distilled water by dissolving the weighed amounts of the samples. The ionic strength of the medium was kept constant with the help of standard solution of potassium chloride. The method gave reproducible results.

Oxalic and acetic acids, found as the common product of oxidation of these diols, was identified by paper chromatographs.

### RESULTS AND DISCUSSION

In the present studies, the kinetics of oxidation of pinacol and pinacol hydrate by hexacyanoferrate (III) in presence of sodium hydroxide is made. It has been observed that the order of the reaction is unity with respect of hexacyanoferrate (III) ion even upto tenfold variation (Fig. 1), which is obvious on plotting  $-dc/dt$  against hexacyanoferrate (III) concentration. The values of  $-dc/dt$  have been calculated from the initial slope of the curve obtained on plotting the remaining hexacyanoferrate (III) concentration against time in order to avoid the possible errors involved

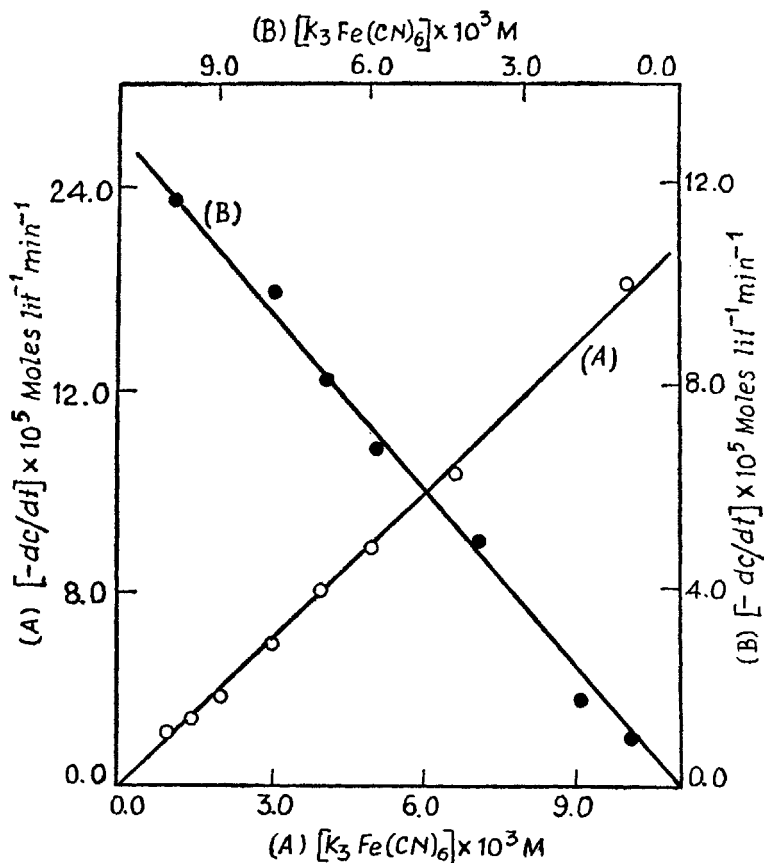


FIG. 1. (A) [PINACOL] =  $4.0 \times 10^{-2} M$   
 [NaOH] = 0.3M  
 (B) [PINACOL HYDRATE] = 0.04M  
 [NaOH] = 0.5M

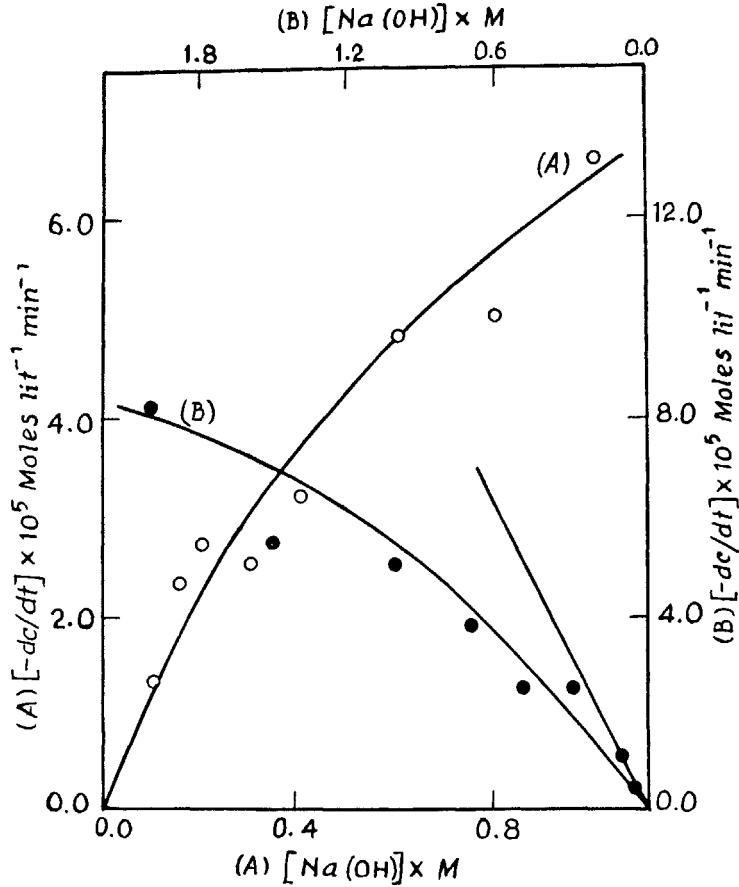


FIG. 2. (A)  $[K_3 Fe (CN)_6] = 2.0 \times 10^{-3} M$   
 $[PINACOL] = 0.04 M$   
 (B)  $[K_3 Fe (CN)_6] = 2.0 \times 10^{-3} M$   
 $[PINACOL HYDRATE] = 0.04 M$

due to intervention of the products. (The typical curve is given in Fig. 2 for both the substrates). The exact dependence of the reaction rate on hydroxyl ion and the organic substrate (Pinacol and pinacol hydrate) shown graphically in Figs 3 and 4. These figures clearly indicate that the reaction rate follows a first-order dependence on the low concentration of alkali and organic substrate and tend towards zero order kinetics at their higher concentrations. In order to avoid the possible intervention involved due to the ionic strength, all the experimental measurements were made at constant ionic strength medium.

Thus, the above data indicates that the rate law is

$$\frac{-d [Fey]}{dt} = k [Fey] [G] [OH^-], \quad \dots (1)$$

when hydroxyl ion and the substrates concentration is very low. In the above equa-

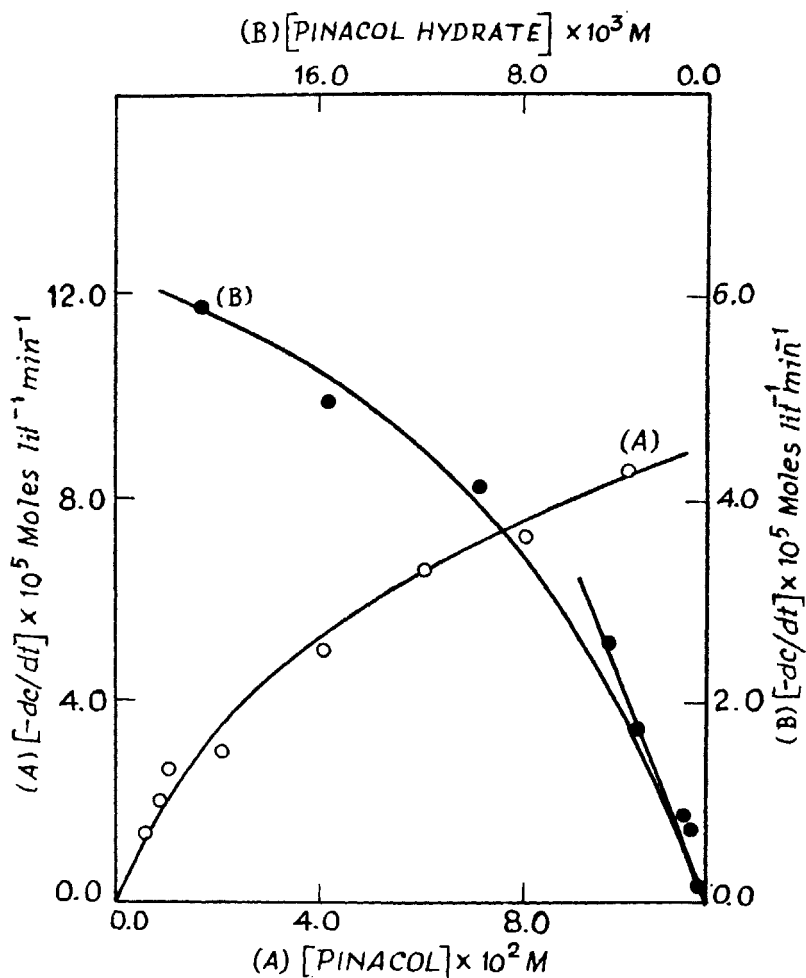
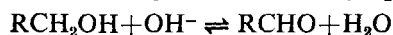


FIG. 3.  $[K_3 Fe (CN)_6] = 2.0 \times 10^{-3} M$   
 $[NaOH] = 1.0 M$

(B)  $[K_3 Fe (CN)_6] = 2.0 \times 10^{-3} M$   
 $[NaOH] = 2.0 M$

tion 'G' stands for pinacol or pinacol hydrate, 'Fey' for hexacyanoferrate (III) and 'k' stands for specific rate constant.

A little detailed information available on the glycol permanganate (cf. Stewart 1965) reaction in alkaline medium, it is possible that a cyclic ester is an intermediary in this case, as it is with chromic acid (Heidt *et al.* 1945) and lead tetra acetate (Crige 1934; and Bell *et al.* 1958) glycol cleavage reactions. In the alkaline permanganate oxidation of alcohols, the base catalysis, however, is clearly due to the ionization of alcohol according to the following equation :



Similarly, in the present case, the base catalysis might be assumed due to ionization of alcoholic group of the diols.

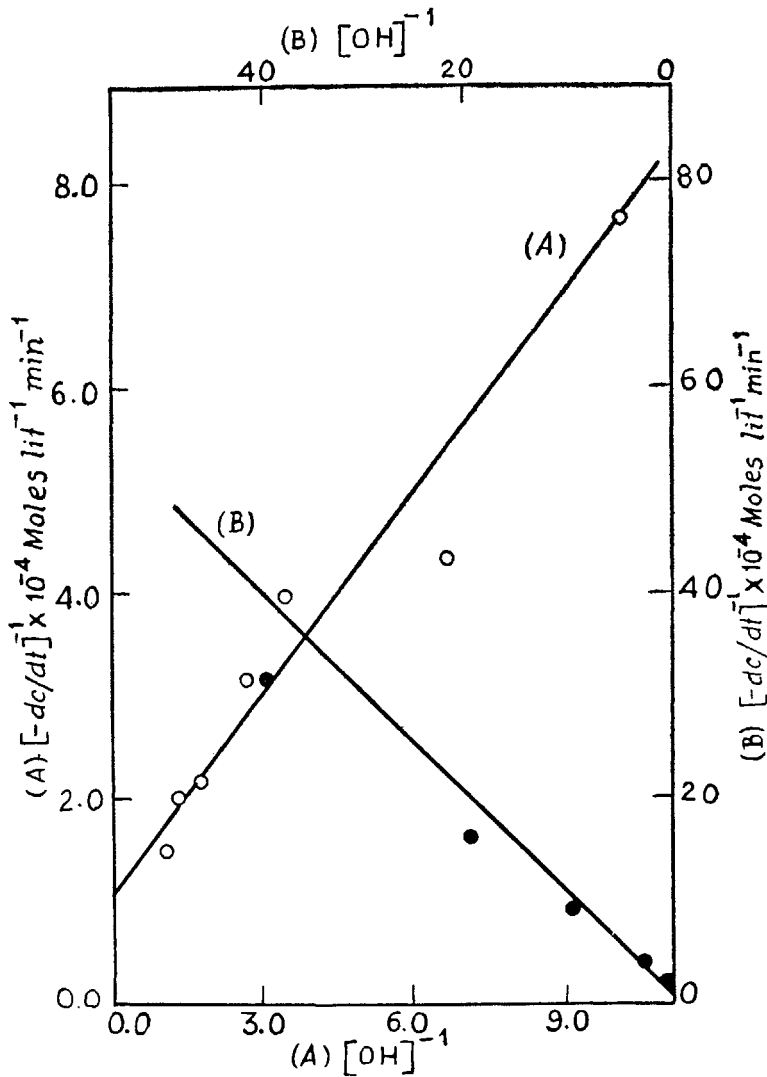
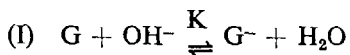
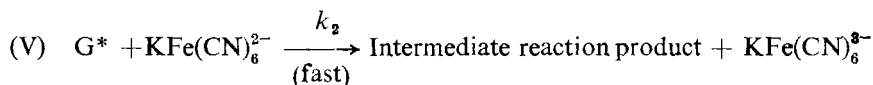
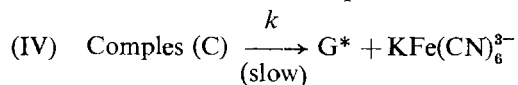
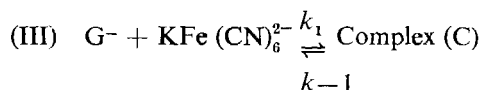
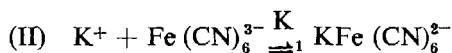


FIG. 4. (A)  $[K_3Fe(CN)_6] = 2.0 \times 10^{-3}M$   
 $[PINACOL] = 4.0 \times 10^{-2}M$   
 (B)  $[K_3Fe(CN)_6] = 2.0 \times 10^{-3}M$   
 $[PINACOL\ HYDRATE] = 4.0 \times 10^{-2}M$

In the hexacyanoferrate (III) oxidation of the organic compounds, the general mode has invariably been described *via* a direct charge transfer process. However, in most of the reactions, the retarding effect of the organic substrate has been reported. In the enzyme catalysed reactions, the retarding effect of the organic substrate corresponding to the plot made in Fig. 4 indicating the complex forming step involved in the process has already been observed. Thus on the basis of these results the following probable steps might be proposed :—





The formation of the  $KFe(CN)_6^{3-}$  anion in step II is reported by several workers and it has been found that equilibrium lies well towards right (Easton *et al.* 1967; Singh, M. P. & Nath, N. 1962; and Singh H. S. 1963).

Now the rate law might be formulated in terms of the decreasing hexacyanoferrate (III) concentration :—

$$-\frac{d[FeY]}{dt} = k_{-1} [\text{complex}] + k_{-1} [G^*] [KFe(CN)_6^{2-}] \quad \dots (2)$$

Now considering the steady state condition and the total hexacyanoferrate (III) by the equation,

$$[Fe(CN)_6^{3-}]_T = [Fe(CN)_6^{3-}] + [KFe(CN)_6^{2-}] + [\text{complex}], \quad \dots (3)$$

where  $T$  refers to the total.

The final rate law will be in the following form :—

$$-\frac{d[FeY]}{dt} = \frac{2k k_1 K [K^+] [G] [OH^-] [FeY]_T}{(k + k_{-1}) \{ [1 + K_1 [K^+]] + k_1 K K_1 [K^+] [G] [OH^-] \}} \quad \dots (4)$$

The rate Eq. (4) accounts for the variation of the order of reaction with respect to hydroxide ion and to organic substrate. The first order kinetics with respect to hexacyanoferrate (III) concentration is also quite obvious.

Since it is reported that the step II of the proposed scheme lies mainly towards right and thus it might be assumed that  $K_1 [K^+] \gg \gg 1$  and the Eq. (4) reduces to Eq. (5)

$$-\frac{d[FeY]}{dt} = \frac{2k k_1 K [G] [OH^-] [FeY]_T}{(k + k_{-1}) + k_1 K [G] [OH^-]} \quad \dots (5)$$

Now at very low concentrations of hydroxyl ion and diols, the inequality  $(k + k_{-1}) \gg k_1 K [G] [OH^-]$  will hold good, because in this condition the values of  $k_1$  and  $K$  will be very small as compared to  $(k + k_{-1})$ . So the Eq. (5) reduces to

$$v_t = -\frac{d[FeY]}{dt} = \frac{2k k_1 K}{k + k_{-1}} [G] [OH^-] [FeY]_T, \quad \dots (6)$$

TABLE I

Name of diol	$\frac{k + k_{-1}}{kk_1 K}$	Variation
Pinacol	1.21	Pinacol
	1.14	OH <sup>-</sup>
Pinacol hydrate	1.33	Pinacol hydrate
	1.52	OH <sup>-</sup>

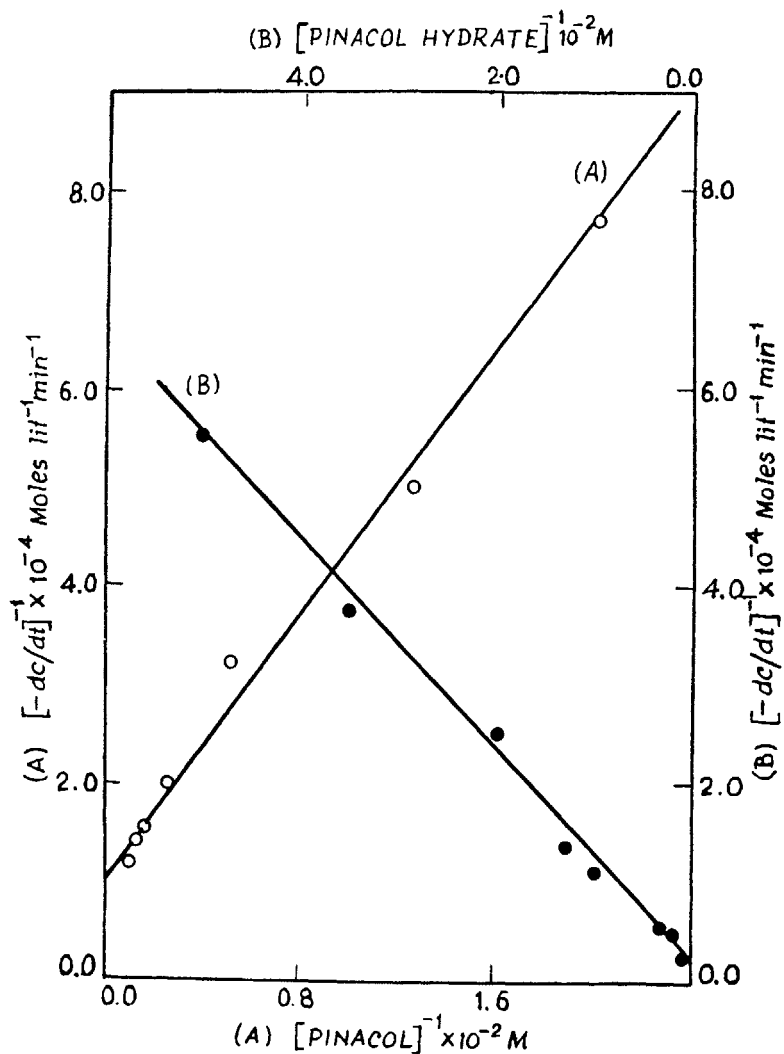


FIG. 5. A  $[K_2 Fe (CN)_6] = 2.0 \times 10^{-3} M$   
 $[NaOH] = 1.0 M$   
 (B)  $[K_2 Fe (CN)_6] = 2.0 \times 10^{-3} M$   
 $[NaOH] = 2.0 M$

Now the rate law (6) clearly explains the first order kinetics with respect to hexacyanoferrate (III), hydroxyl ion and organic substrates at their low concentrations. Thus it clearly supports the reaction mechanism at low concentration of hydroxyl ion and organic substrates. So the values of  $(k + k_{-1})/2kk_1 K$  were calculated from the straight line portions of Figs. 3 and 4 (i.e., at very low concentration of hydroxyl ion and organic substrates). These values are given in Table I. A perusal of this table clearly substantiates that these values, obtained from two different methods (i.e., from hydroxyl ion and organic substrates variation) are quite close to each other. Thus the rate law (6) again supports the reaction mechanism. At higher concentration of hydroxyl ion and organic substrates the value of  $k_1 K[G] [OH^-]$  will be quite large and thus the retarding trend of hydroxyl ion and organic substrates would be obtained and the inequality  $k + k_{-1} \gg k_1 K [G] [OH^-]$  will not be valid and therefore, at higher hydroxyl ion and diols concentration further verification of the rate expression would be made by rewriting as

$$\frac{1}{v_4} = \frac{k + k_{-1}}{2kk_1 K[G] [OH^-] [Fe(CN)_6^{3-}]} + \frac{1}{2k [Fe(CN)_6^{3-}]} \quad \dots (7)$$

The Eq. (7) clearly indicates that, if a plot is made between  $1/\text{Rate}$  and  $1/[OH^-]$  or  $1/[G]$ , certainly a straight line with positive intercept at  $y$ -axis will be obtained. From the slope and intercept of these plots (Fig. 5) the values of  $k + k_{-1}/kk_1 K$  and  $k$  are calculated (Table II). A perusal of Table II again indicates a close similarity between the values of  $(k + k_{-1})/kk_1 K$  which are obtained from two different methods (i.e., by diol and hydroxyl ion variation). It also supports the validity of rate law (5) on comparing the values of  $k + k_{-1}/kk_1 K$  given in Tables I and II. It again substantiates that these values are quite similar to each other so the proposed reaction mechanism appears to be quite probable.

TABLE II

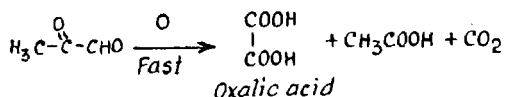
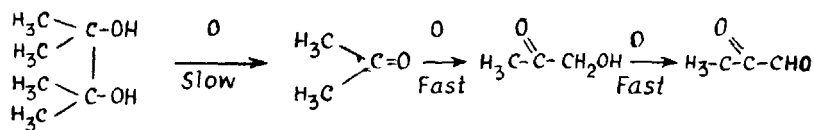
Name of diol	$\frac{k + k_{-1}}{kk_1 K}$	Variation $k$
Pinacol	1.32	$2.50 \times 10^{-3}$ Pinacol
	1.12	$2.50 \times 10^{-3}$ $OH^-$
Pinacol hydrate	1.12	$1.00 \times 10^{-2}$ $OH^-$
	1.96	$1.00 \times 10^{-2}$ Pinacol hydrate

A close examination of the values of  $k$  obtained from two methods in pinacol and pinacol hydrate, clearly indicates that the rate of complex disproportionation for the pinacol is faster than the pinacol hydrate. This difference in rate might be due to difference in molecular weight of two compounds because pinacol hydrate contains six molecules of water as a water of crystallization in pinacol. The product study also indicates the formation of oxalic acid as the final oxidation product in both the compounds. Thus the rate of complex disproportionation and the product study clearly reveals that both the compounds are the same with the difference of six molecules of water of crystallisation in Pinacol hydrate.

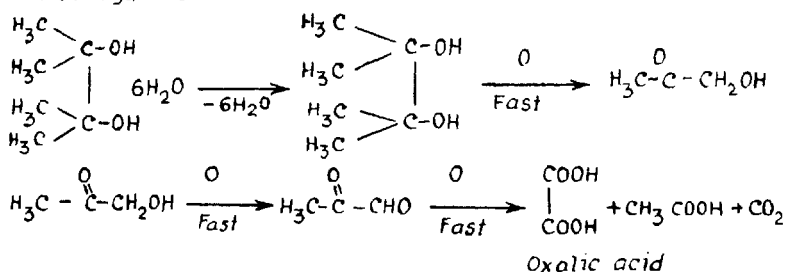


Now on the basis of the final oxidation product the actual steps might be proposed for the oxidation of Pinacol and Pinacol hydrate as follows:—

Pinacol



Pinacol hydrate



The presence of oxalic acid and acetic acid has been confirmed by chromatographic method of analysis.

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