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OXIDATION OF ALDEHYDES WITH PERMANGANATE IN ACIDIC AND ALKALINE MEDIA

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The oxidation mechanism of aldehydes with permanganate was studied in acidic and alkaline media on acetaldehyde, propionaldehyde, pivalaldehyde (2,2′-dimethylpropanal) and chloral substrates. On addition of water to acetaldehyde dissolved in organic solvents the rate increased, and therefore it may be stated that the hydrate form is more reactive than the aldehyde form. Acid-catalysed nucleophilic addition of permanganate is suggested. In alkaline medium a mechanism based on electron abstraction from the alkoxy anion of the hydrate is proposed. Deprotonation constants of hydrate could be calculated.. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Although several studies have been made on the oxidation mechanism of aldehydes,[1–26] the reaction cannot be considered as fully clarified. It is still an open question, for example, which of the two main types of carbonyl reactions the oxidation of aldehydes can be associated with: nucleophilic addition or nucleophilic substitution on the carbon atom in the α-position. The question is all the more complicated since in aqueous medium simple aldehydes are considerably hydrated.

Previously, enolization was generally regarded as the rate-determining step;[1, 2] later, however, this idea was discarded since the rate of oxidation with practically all effective oxidizers proved to be orders of magnitude faster than that of enolization. Most recently, aldehyde hydrate has been considered[3–5, 7–18] to be the more reactive form, since in this case the rate constant of the almost fully hydrated formaldehyde can be fitted to Taft's straight line. With the use of various oxidants, mechanisms based on hydride ion (H^-) abstraction,[3–13] H-atom abstraction from the C–H bond[14] or from hydrate-OH,[15, 16] esterification[17, 18] and complex formation[19] have been assumed.

As regards oxidation by permanganate, in connection with furfural, Freeman *et al.*[20] stated that no distinction can be made between the two mechanisms: H^- abstraction from the hydrate or nucleophilic attack on the aldehyde form. Later, however, in connection with pivaldehyde,[21] they gave preference to the latter form, in contrast to Banerji,[10–12] who maintained that the first variation was more probable. Most recently, in connection with glycol aldehyde, the possibility of enolization has arisen again,[22a] in spite of the fact that according to some workers[22b] enolization proceeds slowly in the case of glycol aldehyde also.

In acidic solution, the product proved to be the corresponding carboxylic acid. In the oxidation of acetaldehyde in alkaline medium, oxalic acid was observed in addition to acetic acid by previous workers.[23] In any case, based on ^{18}O-studies, it may be considered as verified that the O atom is transferred to the product in acidic and neutral media from MnO_4^- and in alkaline medium from water.[20, 24]

The conflicting ideas on the mechanism and the contrasting interpretations of the role of $[H^+]$ and $[OH^-]$ seemed to justify further investigations on the topic. In this work, acid- and base-catalysed oxidations of acetaldehyde, propionaldehyde, pivalaldehyde (2,2′-dimethylpropanal) and chloral were studied. For the sake of comparison, our previous results obtained with formaldehyde[25] and glycoaldehyde[26] were also taken into consideration.

RESULTS AND DISCUSSION

Stoichiometry and products

In acidic medium, the reduction product of permanganate is Mn^{3+}, which can be maintained in solution even at pH 6·8 by prior addition of pyrophosphate ion and determined spectrophotometrically. The $Mn(H_2P_2O_7(_3^{3-}$ complex ion reacts with aldehydes orders of magnitude more slowly than

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Table 1. Dependence of pseudo-first order rate constants on the substrate concentration[a]

10^2 [substrate] (mol dm^{-3})	Acetaldehyde	Propionaldehyde	Pivalaldehyde	Chloral
1	0·90 (76)	2·60 (170)	5·42 (6·4)	0·0118[b] (7·67)
2	1·87 (149)	5·35 (357)	10·4 (13·1)	0·0231[b] (15·2)
3	2·59 (234)	7·72 (485)	15·6 (18·9)	0·0364[b] (23·2)
4	3·49 (301)	10·3 (706)	22·5 (26·1)	0·0463[b] (30·5)
5	4·63 (382)	13·1 (822)	27·9 (31·4)	0·0596[b] (38·5)

[a] $[MnO_4^-] = 1\cdot0\times10^{-3}$ mol dm^{-3}; $I = 2\cdot0$ mol dm^{-3}; $T = 25$ °C. $10^2 k^a_{obs}(s^{-1})$ values at $[HClO_4] = 0\cdot25$ and $[Na_4P_2O_7] = 5\times10^{-3}$ mol dm^{-3}. $10^2 k^b_{obs}(s^{-1})$ values in parentheses at [NaOH] = 0·20 mol dm^{-3}.

[b] At a tenfold chloral concentration.

permanganate, and therefore Mn^{3+} may be considered as the end product. By iodimetric determination of the excess of permanganate, it could be established that in each case two-electron oxidation took place, involving the formation of corresponding carboxylic acids. In the case of acetaldehyde, acetic acid was removed from the system by distillation and obtained in 98·6% yield.

The stoichiometric equation is thus

$$2RCHO + MnO_4^- + 4H^+ \rightarrow 2RCOOH + Mn^{3+} + 2H_2O$$

In alkaline solution, if $[OH^-] \geq 0\cdot1$ mol dm^{-3}, then in the first step permanganate is reduced only to MnO_4^{2-}, the reaction of which is rather slow. Also in this case, oxidation proved to be two-electron; accordingly, no oxalic acid could be detected as the oxidation product of acetaldehyde. The stoichiometric equation here is

$$RCHO + 2\ MnO_4^- + 3OH^- \rightarrow RCOO^- + 2\ MnO_4^{2-} + 2HO$$

Kinetics

Kinetic investigations were carried out with a large excess of the substrate under apparent first-order conditions and permanganate consumption was followed by spectrophotometry. In each case the plots of $\log(A - A_\infty)$ versus time gave a straight line, indicating that the reaction has a first-order dependence on permanganate (A = absorbance at 524 nm). Table 1 gives the k_{obs} values calculated from the slopes of the straight lines, which are in direct proportion to substrate concentration; thus, the reaction also shows a first-order dependence on the substrate. The corresponding second-order rate constant values are given in Tables 2 and 4.

Table 2. Dependence of apparent second-order rate constants (k^a dm^3 mol^{-1} s^{-1}) on hydrogen ion concentration and the activation parameters[a]. Rate constants of non-catalysed (k_0) and acid-catalysed (k_H) processes [equation (1)].

$[H^+]$ (mol dm^{-3})	Formaldehyde[c]	Acetaldehyde	Propionaldehyde	Pivalaldehyde	Chloral	Glycolaldehyde[d]	Ethanol[c]
1·0	1·12	2·42	6·13	10·3	$1\cdot92\times10^{-3}$	1·88	$5\cdot76\times10^{-3}$
0·75	0·83	1·88	4·95	8·9	$1\cdot70\times10^{-3}$	1·41	$4\cdot62\times10^{-3}$
0·50	0·54	1·45	3·84	7·2	$1\cdot46\times10^{-3}$	0·97	$3\cdot31\times10^{-3}$
0·25	0·31	0·90	2·60	5·4	$1\cdot18\times10^{-3}$	0·55	$2\cdot22\times10^{-3}$
0·10	0·125	0·61	1·79	4·0	$1\cdot07\times10^{-3}$	0·31	$1\cdot45\times10^{-3}$
0·05	0·082	0·48	1·55	3·6	$1\cdot01\times10^{-3}$	0·185	$1\cdot31\times10^{-3}$
pH 2·4	0·027	0·41	1·35	3·2	$0\cdot97\times10^{-3}$	0·160	$1\cdot12\times10^{-3}$
pH 4·8	0·008	0·39	1·10	3·1	$0\cdot94\times10^{-3}$	0·140	$1\cdot09\times10^{-3}$
pH 6·6	0·008	0·39	1·10	3·1	$0\cdot94\times10^{-3}$	0·135	$1\cdot11\times10^{-3}$
0·1[b]	0·158	0·71	2·21	4·4	$1\cdot17\times10^{-3}$	0·39	$1\cdot62\times10^{-3}$
K_{hy}	1820	1·20	0·71	0·24	$2\cdot8\times10^4$	9·1	0
k_0 (M^{-1} s^{-1})	0·008	0·39	1·10	3·1	$0\cdot94\times10^{-3}$	0·14	$1\cdot09\times10^{-3}$
k_H (M^{-2} – s^{-1})	1·08	2·01	5·03	7·2	$0\cdot98\times10^{-3}$	1·74	$4\cdot60\times10^{-3}$
$\Delta H^{\neq}$ (kJ mol^{-1})	—	58·6	54·6	37·8	—	—	—
$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	—	− 41	− 46	− 62	—	—	—

[a] $[Substrate]_0 = 1\cdot00\times10^{-2}$ mol dm^{-3}; $[MnO_4^-] = 1\cdot0\times10^{-3}$ mol dm^{-3}; $[Na_4P_2O_7] = 5\times10^{-3}$ mol dm^{-3}; $I = 2\cdot0$ mol dm^{-3}; $T = 25$ °C.

[b] Ionic strength 0·1 mol dm^{-3}.

[c] Ref. 25.

[d] Ref. 26.

Table 3. Dependence of acetaldehyde k_0 values ($dm^3\ mol^{-1}\ s^{-1}$) on the water content of organic solvents

Water (%v/v)	DMF[a]	Diglyme	Acetone
0	0·090	0·085	0·072
10	0·137	0·130	0·116
20	0·18		
30	0·21		
40	0·24		
50	0·27		
100	0·39		

[a] $[Na_4P_2O_7]=3\times10^{-3}$ mol dm^{-3}

Kinetics in acidic solution

Measurements were performed over the range $[H^+]=0{\cdot}05$–$1{\cdot}0$ mol dm^{-3} and at pH 2·4, 4·6 and 6·8. Based on the relevant data in Table 2, it is evident that the k^a value is linearly dependent on $[H^+]$, i.e. the kinetic equation is

$$-\frac{d[MnO_4^-]}{dt}=k^a_{obs}[MnO_4^-]=k^a[A]_T[MnO_4^-]$$

$$=(k_0+k_H[H^+])[A]_T[MnO_4^-] \qquad (1)$$

where $[A]_T$ is total aldehyde concentration.

Enolization cannot play a role here, because of the low values of pK_{en} (p$K_{en}=4{\cdot}66$–$6{\cdot}66$ for acetaldehyde[27–30] and 3·91 for propionaldehyde,[27–28] where K_{en} = [enol]/[aldehyde]), and because the rate constants of enolization in acidic solution[28–30] ($k_{en}=1{\cdot}65\times10^{-5}$ and $1{\cdot}88\times10^{-5}$ dm^3 mol^{-1} s^{-1}, respectively) are negligible compared with the rate constants of oxidation. Pivalaldehyde and chloral are incapable of forming an enol form.

At the same time, aldehydes in aqueous solution are considerably hydrated. Table 2 gives the most probable data for K_{hy} = [hydrate]/[aldehyde] available in the literature.[31–43] Hydration in acidic solution is rapid compared with oxidation ($k_H=500$–800 dm^3 mol^{-1} s^{-1} for acetaldehyde[31, 32, 36, 38, 41] and 450–490 dm^3 mol^{-1} s^{-1} for propionaldehyde[32, 36, 41]), i.e. the kinetic equation does not show whether the aldehyde or the hydrate is the reactive form.

Apparently, the dependence of k^a on $[H^+]$ can hardly be due to the equilibrium $H^+ + MnO_4^- \rightleftharpoons HMnO_4$ as suggested by Banerji,[10–12] since under these conditions permanganate must be completely deprotonated (p$K=-2{\cdot}25$).[13, 44, 45] Considering the fact that aldehyde reactions are generally acid- and/or base-catalysed, it seems reasonable to assume acid catalysis also in the case of oxidation. With a reduction in ionic strength the k^a value in each case slightly but definitely increased; therefore, reactions with inversely charged molecules must be taken into account. The corresponding rate constants of ethanol[25] are also listed in Table 2. As is evident from the data, acid catalysis occurs also in the case of ethanol. This suggests that proton addition of the alcoholic hydroxyl group and consequently that of the

Table 4. Dependence of apparent second-order rate constants (k^b dm^3 mol^{-1} s^{-1}) on hydroxyl ion concentration and the activation parameters[a]. Measured K^b_{Hy} deprotonation constants of hydrates [equation (3)] and k_{Hy^-} rate constants of hydrate anions [equation (4)].

$[OH^-]$ (mol dm^{-3})	Formaldehyde[c]	Acetaldehyde	Propionaldehyde	Pivalaldehyde	Chloral	Glycolaldehyde[d]
1·0	196	198	613	19·6	7·40	350
0·80	—	181	520	16·1	7·84	—
0·75	160	—	—	—	—	354
0·60	—	155	422	13·5	7·90	—
0·50	121	—	—	—	—	376
0·40	—	126	302	10·1	7·52	—
0·25	79·3	—	—	—	—	374
0·20	—	76	170	6·4	7·67	—
0·10	47·4	44	90	4·8	7·69	365
0·10[b]	24·2	29	51	2·9	3·96	172
K^b_{Hy} (M^{-1})	19 (0·080)[e]	2·88	0·64	Small	Large	Large
k_{Hy^-} ($M^{-2}\ s^{-1}$)	28 (1035)[e]	161	1720	43·3[f]	3·84	183
$\Delta H^{\neq}$ (kJ mol^{-1})	—	39·8	35·7	29·4	—	—
$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	—	−79	−88	−101	—	—

[a] $[Substrate]_0=1{\cdot}00\times10^{-2}$ mol dm^{-3}; $[MnO_4^-]=1{\cdot}0\times10^{-3}$ mol dm^{-3}; $I=2{\cdot}0$ mol dm^{-3}; $T=25$ °C.

[b] Ionic strength 0·1 mol dm^{-3}.

[c] Ref. 25.

[d] Ref. 26.

[e] Deprotonation of the second HO-group.

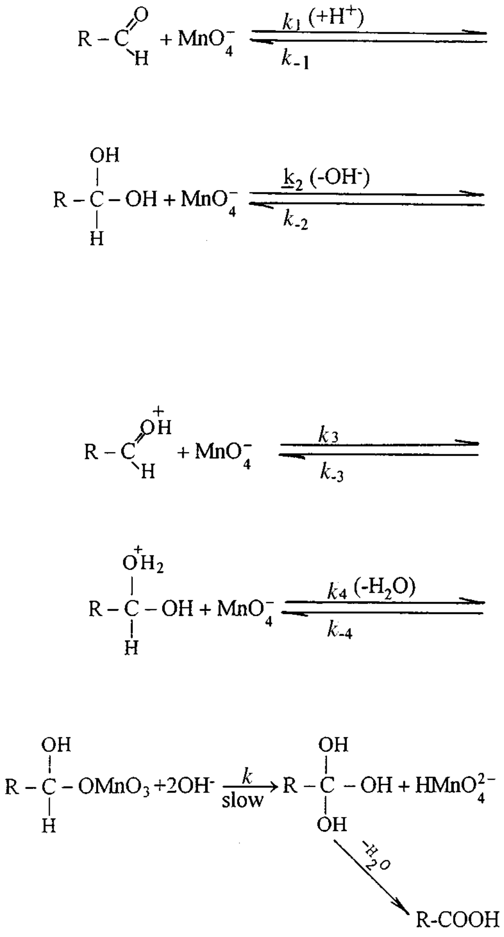
[f] The k_{Hy}–K^b_{Hy} product.

aldehyde hydrate may also take place.

Acetaldehyde can be prepared in a completely hydrate-free form by sulphuric acid decomposition of paraldehyde. The acetaldehyde attained was then distilled to dried dimethylformamide (DMF) and, since DMF satisfactorily dissolves $KMnO_4$, kinetic measurements could also be performed with the pure aldehyde form. On gradually increasing the water content of the reaction mixture to 50%, we observed a considerable (*ca* fourfold) increase in the k_0 value (Table 3) Similar results were attained in diglyme and acetone. Owing to the effect of the medium, the comparison of the rate constants with those obtained in water is only of informative character. Nevertheless, the increase in reaction rate under the influence of water points to the fact that although both forms are capable of reaction, the hydrate has higher reactivity. Positive polarity on the C atom seems to be more intense for the geminal glycol than for the carbonyl group, which is more advantageous for nucleophilic MnO_4^- attack, in spite of the fact that steric conditions are more favourable in the case of the aldehyde owing to its planar structure. Upon acidification, oxidation of the organic solvent is also accelerated; therefore, the k value could not be measured. Comparison with a blank test showed, however, that the oxidation of acetaldehyde was catalysed by acid also under these conditions for both carbonyl and hydrate polarization is enhanced by protonation of their O atom(s).

It can be stated that the nucleophilic attack of MnO_4^- take place on all four species and each proces must give the same permanganate ester as intermediate (Scheme 1). The oxidative decomposition of this ester is the rate-determining step.

The protonation constant for aldehyde (K_{H1}) and that for hydrate (K_{H2}) must be low because of the linear dependence of k^a on [H^+]. On the assumption that the rate constant of the reverse processes in Scheme 1 are fast, the steady-state approximation can be applied. The kinetic equation (2) obtained is in accordance with the observed equation (1).



Scheme 1

$$-\frac{d[MnO_4^-]}{dt}=k[E]$$

$$=k\frac{k_1+k_2K_{hy}+k_3k_{H1}[H^+]+k_4K_{hy}K_{H2}[H^+]}{(1+K_{hy})(k_{-1}+k_{-2}+k_{-3}+k_{-4}+k)}[A]_T[MnO_4^-]$$

$$=\left\{k\frac{k_1+k_2K_{hy}}{(1+K_{hy})\sum k}+k\frac{k_3K_{H1}+k_4K_{hy}K_{H2}}{(1+K_{hy})\sum k}[H^+]\right\}[A]_T[MnO_4^-]$$

$$=(k_0+k_H[H^+])[A]_T[MnO_4^-] \qquad (2)$$

The proposed mechanism explains the effect of structure on reactivity: the electron-releasing group stabilizes the permanganate ester, increasing its equilibrium constants, and also it directly raises the constant of oxidative decomposition k due to promotion of electron abstraction by permanganate.

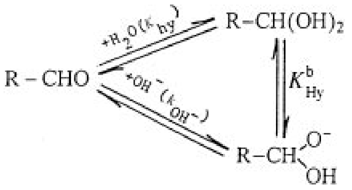
The thermodynamic parameters also presented in Table 2 are not very characteristic, considering the fact that the k^a values measured are composed of several rate and equilibrium constants. Owing to proton elimination involved in oxidative decomposition of ester, a charge occurs in the activated complex, therefore an increase in solvation must be taken into consideration. This accounts for the relatively high negative $\Delta S^{\neq}$ values.

Since a two-electron oxidation step is involved, the first reduction product of permanganate is $Mn(V)O_4^{3-}$, the further fate of which is determined by two possibilities. As is well known,[45–48] in acidic solution the disproportionation of Mn(V) is fairly rapid. According to more recent studies,[49] however, in acidic solution Mn(V) is capable of extremely rapid reaction with some groups of the substrates, hence also with aldehydes, therefore, this possibility cannot be excluded either.

Kinetics in alkaline solution

Measurements were carried out in the range $[OH^-]=0{\cdot}1$–$1{\cdot}0\ mol\ dm^{-3}$. Under these conditions, in the first step, permanganate is reduced only to manganate. It cannot, however, be unambiguously determined whether two consecutive one-electron steps take place or if hypomanganate is formed in a two-electron step and then oxidized into manganate by permanganate in a fast reaction. The latter assumption is more probable since the reaction products do not point to a radical mechanism.

In alkaline solution the rate constant of enolization is also low[50] ($k=7{\cdot}8\times10^{-2}\ dm^3\ mol^{-1}\ s^{-1}$ for acetaldehyde) related to the rate constant of oxidation, which implies that enolization cannot play a significant role under these conditions either. Deprotonation on the C-atom in the α-position can also be neglected ($pK_a=16{\cdot}8$–$19{\cdot}7$ for acetaldehyde).[50–52] These phenomena are in conformity with the observation that the corresponding carboxylic acids are formed also in alkaline solution, i.e. no oxidation takes place on the C-atom in the α-position. In alkaline solution hydrate anion formation must be taken into consideration. The following equilibria are valid:

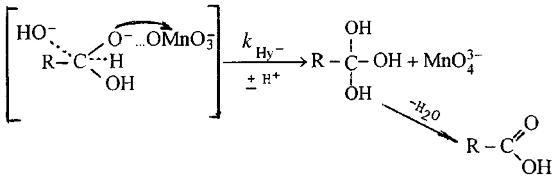


where

$$K^b_{Hy}=\frac{[RCH(OH)O^-]}{[RCH(OH)_2][OH^-]} \qquad (3)$$

Equilibrium sets in quickly owing to the high rate constant of OH^- nucleophilic attack ($k_{OH^-}=2{\cdot}65-8{\cdot}0\times10^4\ dm^3\ mol^{-1}\ s^{-1}$).[31, 35]

In connection with alcohols, it has been proved that the alkoxy anion is the reactive form[26] and oxidation proceeds via direct electron withdrawal and simultaneous nucleophilic attack of the hydroxy ion. By applying the mechanism to hydrate, for the activated complex we obtain the following form:



The kinetic equation is

$$-\frac{d[MnO_4^-]}{dt}=k^b_{obs}[MnO_4^-]=k^b[A]_T[MnO_4^-]$$

$$=2\frac{k\dfrac{k_1+k_2K_{hy}}{\sum k}+k_{Hy^-}K_{hy}K^b_{Hy}[OH^-]}{1+K_{hy}+K_{hy}K^b_{Hy}[OH^-]}\times[A]_T[MnO_4^-] \qquad (4)$$

$$=2\frac{(1+K_{hy})k_0+k_{Hy^-}K_{hy}K^b_{Hy}[OH^-]}{1+K_{hy}+K_{hy}K^b_{Hy}[OH^-]}\times[A]_T[MnO_4^-]$$

where k_{Hy^-} is the rate constant of the hydrate anion. The factor of 2 points to fast consumption of another MnO_4^- molecule after the rate-determining step. k^b increases with increase in ionic strength in accordance with the assumption that the reaction occurs between ions of identical sign.

For K_{hy} we applied literature data[31–43] (given in Table 2); k_0 is the rate constant measured in neutral media, and therefore the two-parameter fitting of

$$k^{b} = 2\,\frac{(1+K_{hy})k_0 + k_{Hy^-}K_{hy}K^{b}_{Hy}[OH^-]}{1+K_{hy}+K_{hy}K^{b}_{Hy}[OH^-]} \qquad (5)$$

was applied. The results are summarized in Table 4. In the case of glycol aldehyde and chloral, the k^b value does not depend on $[OH^-]$, i.e. these substrates are completely deprotonated over the whole range (which is in correspondence with literature data, according to which $pK_a = 14 - \log K^{b}_{Hy} = 10{\cdot}04$ for chloral).[53] In the case of formaldehyde, fitting could be carried out only if deprotonation of the second HO group was also taken into account. In the case of pivalaldehyde, k^b was linearly dependent on $[OH^-]$, i.e. deprotonation was so slight that only the product of the two constants could be attained by fitting. For acetaldehyde, K^{b}_{Hy} was in correspondence with literature data[42, 53, 54] attained by other methods. This may be considered as decisive evidence in support of the mechanism proposed.

It is a much debated question and has still not been clarified whether the permanganate oxidation of an alkoxy anion takes place by electron withdrawal simultaneously with proton elimination and hydroxy ion entry or by hydride ion abstraction. Both the simple and E_s-corrected Taft plots for k_0 and k_{Hy^-} showed curvature, but regarding their trend it may be stated that with increase in σ^*, $\log(k/k_{A1})$ decreases, which implies that the electron density of the reaction center is lower in the activated complex than in the initial state (k_{A1} is the rate constant of acetaldehyde, for which $\sigma^* = 0$). On the basis of the above, it cannot be decided actually which of the two mechanisms takes place. The activation parameters do not supply definite evidence either, as for both pathways high negative $\Delta S^{\neq}$ values are to be expected. Since, however, toluene, which is bound to be oxidized via H^- abstraction,[55] reacts by about five to six orders of magnitude slower than the alkoxy anion, electron withdrawal seems to be more probable.

In conclusion, it can be established that permanganate oxidation of aldehydes takes place according to two mechanisms. In acidic medium acid-catalysed nucleophile addition of permanganate anion occurs and the hydrate is more reactive than the aldehyde form. In alkaline medium, however, electron abstraction from the hydrate anion is the main process.

EXPERIMENTAL

The reagents $KMnO_4$, $HClO_4$, $NaClO_4$ and NaOH were of analytical grade from Merck. Acetaldehyde and paraldehyde (Merck), propionaldehyde and pivalaldehyde (Aldrich) were purified by distillation and intermediate fractions were used. Chloral hydrate was of grade from purum Fluka. Dimethylformamide, diglyme and acetone (Reanal) were dried with 4A molecular sieves.

Stoichiometry. In a stoppered bottle $2{\cdot}0 \times 10^{-4}$ mol of substrate was added to 8×10^{-4} mol of permanganate after previous adjustment of a 0·1 or 0·5 mol dm^{-3} acid or alkali concentration in the latter solution. After a reaction time of 1 h, solid KI was added. Then, following acidification by sulfuric acid, the total excess of oxidant was titrated, using thiosulphate solution.

Products. Product analysis was carried out for acetaldehyde at 0·25 mol dm^{-3} acid and alkali concentrations. A 100 cm^3 volume of 0·1 mol dm^{-3} (*ca* 1×10^{-2} mol) permanganate solution was added to 10 cm^3 of 0·1 mol dm^{-3} (1×10^{-3} mol) of the substrate. After a 30 min reaction time, the excess oxidation capacity was reduced to MnO_2 by hydrazine hydrate. Upon filtration, 50 ml of 85% phosphoric acid was added to the solution, which was distilled until dripping ceased. After the addition of 50 ml of water (2 ×) distillation was continued. The acetic acid content of the distillate was determined by alkalimetry. No Ca oxalate could be precipitated by a standard method after oxidation in alkaline medium.

Kinetics. The stock solutions of permanganate contained the acid or alkali. By this means the effect of aldol dimerization was avoidable. Aldol dimerization is slow[54, 56, 57] in comparison with oxidation.

The concentration of H^+ was adjusted with $HClO_4$ or to Britton–Robinson buffers. Pyrophosphate ions were applied to avoid the disproportionation of Mn^{3+}. The alkali concentration was adjusted with NaOH and $NaClO_4$ to maintain the ionic strength. Kinetic measurements were performed on a stopped flow reaction analyser (Applied Photophysics Bio Sequental SX·17 MV). Each k_{obs} value was obtained as the average values of five individual measurements. The standard deviation of k_{obs} fittings, up to three half times, were lower than 0·1. The estimated accuracy of k_0, k_H, k_{Hy^-} and K^{b}_{Hy} values was ±3% and that of the activation parameters was ±5%. The correlation coefficients of k_{obs} vs $[A]_T$ plots were 0·96.

For the activation parameter measurements the k values were determined in the interval 15–40 °C (in 5 °C steps) at $[H^+] = 0{\cdot}1$ and $[OH^-] = 0{\cdot}25$ mol dm^{-3}. The correlation coefficients of Arrhenius plots ranged between 0·91 and 0·94.

The acetaldehyde obtained by decomposition of paraldehyde was directly distilled into the corresponding solvent cooled with ice. The quantity was determined by weight measurements, and the stock solution was prepared by dilution. Water was added to both stock solutions. Kinetic measurements were carried out on a Hewlett-Packard spectrophotometer (Model 8452A) coupled to a laboratory-made rapid mixing device.

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