Kinetics and mechanism of the oxidation of ketones with permanganate ions

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The kinetics and mechanism of the oxidation of ketones with permanganate ions were studied in aqueous acidic and alkaline media for acetone, hydroxyacetone, butan-2-one and butane-2,3-dione. Acid catalysed nucleophilic addition of the permanganate to the carbonyl C-atom is suggested. In alkaline media, parallel with electron abstraction from the enolate, a concerted mechanism is proposed. Intermediates and end products were determined. Comparisons between halogenation and oxidation have been made.

Introduction

The oxidation mechanism of ketones cannot be regarded as fully clarified either for permanganate or for other oxidants. It is still an open question, which of the two main types of carbonyl reactions (nucleophilic addition or substitution on the α-C-atom) is associated with oxidation, therefore further study of the problem is required. With this in view, we studied the permanganate oxidation of aldehydes.[1] Another important reason for solving this problem is that carbonyl compounds are generally intermediates in oxidation reactions. The presence of ketones may be expected not only in the oxidation of secondary alcohols but also in that of triple bonds.

In acidic media enolization of ketones is generally assumed to be the rate determining step for various oxidants,[2–9] in some cases, however, radical mechanisms are proposed.[10–13] There are several different proposals for the mechanism in the case of permanganate as well.[14–18] Banerji and co-workers[16,17] attribute the rate dependence of ketone oxidation on hydrogen ion concentration both to protonation of the permanganate ion and to enolization, while Sen *et al.*[18] assume an intermediate complex formed in fast pre-equilibrium, the slow decomposition of which is the rate determining step.

In alkali media, enolization[19,20] and the formation of radicals[21–23] are also regarded as rate determining steps. As for permanganate, since Wiberg and Geer[24] published their comprehensive study on acetone oxidation in alkali, the decisive role of enolate anion has been accepted in various reviews as well.[25,26] In the meantime, however, the process of both acid and base catalysed enolization has been examined thoroughly, and the results attained suggest a rather different mechanistic interpretation of this oxidation.

Results and discussion

Acidic media

In the case of the substrates studied (acetone, hydroxyacetone, butan-2-one, butane-2,3-dione) the reaction was strictly first order with respect to both permanganate (Table 1) and substrate concentration. The rate constant observed varied linearly with $[H^+]$ as shown in Table 2. Thus, the observed

Table 1 Dependence of initial slope of permanganate consumption on initial permanganate concentration[a]

$[MnO_4^-]_0/10^3$ mol dm^{-3}	Acetone	Hydroxyacetone	Butan-2-one	Butane-2,3-dione
	Acidic media[b] $\frac{-d[MnO_4^-]}{[S]_0\,dt}/10^{-6}\ s^{-1}$			
0.5	1.6	22	2.3	2.6
1.0	3.4	46	4.5	5.6
2.0	7.0	97	8.5	12
3.0	11	141	14	16
5.0	17	223	22	29
10.0	35	440	43	57
	Alkali media[c] $\frac{-d[MnO_4^-]}{[S]_0\,dt}/10^{-2}\ s^{-1}$			
0.5	1.3	13	1.2	23
1.0	2.8	27	2.4	44
2.0	5.2	47	5.0	76
3.0	6.4	65	6.8	106
5.0	11.5	94	11.5	165
10.0	19	158	23	287

[a] $[substrate]_0 = 10 \times [MnO_4^-]_0$; $I = 2.0$ mol dm^{-3}; $T = 25$ °C. [b] $[HClO_4] = 0.25$ mol dm^{-3}; $[Na_4P_2O_7] = 3 \times [MnO_4^-]_0$. [c] $[NaOH] = 0.25$ mol dm^{-3}.

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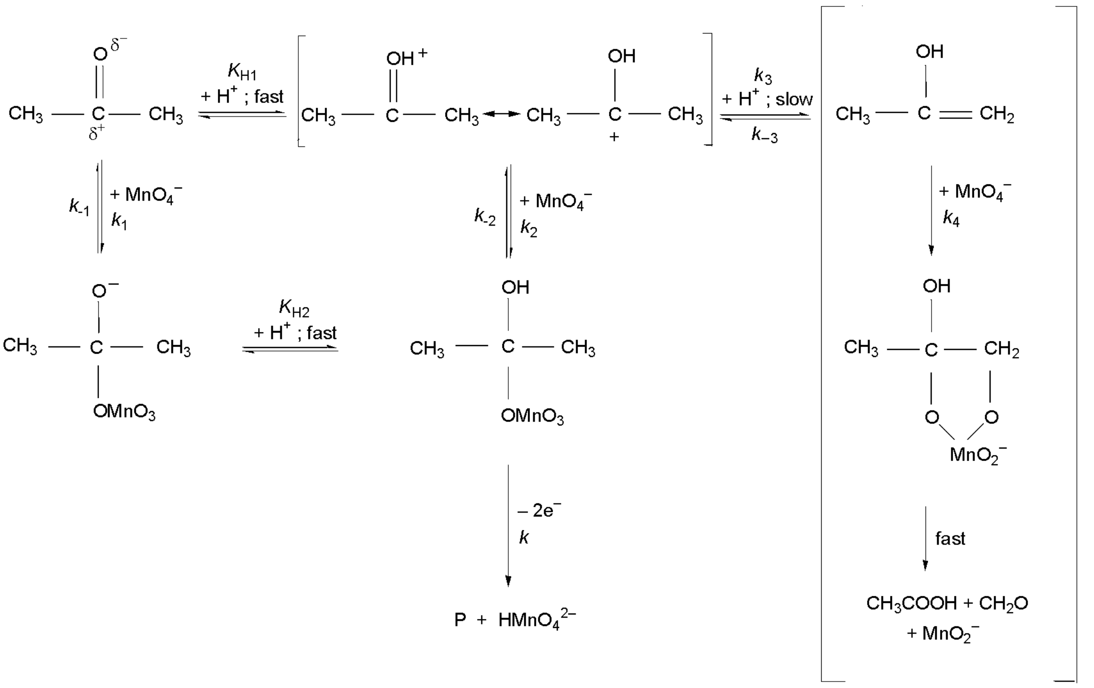
Table 2 Dependence of apparent second-order rate constants (k_A) on hydrogen ion concentration and the activation parameters. Rate constants of non-catalysed (k_0) and acid catalysed (k_H) processes

	$k_A/10^{-3}$ dm^3 mol^{-1} s$^{-1\,a}$			
$[H^+]$/mol dm^{-3}	Acetone	Hydroxyacetone	Butan-2-one	Butane-2,3-dione
0.05	1.8	34	3.0	3.4
0.10	2.3	37	3.2	4.0
0.25	3.4	46	4.5	5.6
0.50	5.3	57	6.0	8.8
0.75	7.5	69	8.1	11.5
1.00	9.8	82	9.9	14.5
pH 4.8	1.3	31	2.6	2.7
0.10^b	3.9	59	6.0	6.1
$\Delta H^‡$/kJ mol^{-1}	45.6	35.9	52.2	40.5
$\Delta S^‡$/J mol^{-1} K^{-1}	−138	−149	−114	−152
$k_0/10^{-3}$ M^{-1} s^{-1}	1.3	31	2.6	2.7
$k_H/10^{-3}$ M^{-2} s^{-1}	8.5	52	7.2	11.8

^{a} [substrate] = 1.0×10^{-2} mol dm^{-3}; $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}; $[Na_4P_2O_7] = 5 \times 10^{-3}$ mol dm^{-3}; $I = 2.0$ mol dm^{-3}; $T = 25$ °C. ^{b} Ionic strength 0.1 mol dm^{-3}.



Scheme 1

kinetic equation is as shown in eqn. (1), where [S] stands for the concentration of ketone (substrate).

$$-\frac{d[MnO_4^-]}{dt} = k_A[S][MnO_4^-] = (k_0 + k_H[H^+])[S][MnO_4^-] \quad (1)$$

For ketones, the degree of enolization is low ($pK_{en} = 8–9$).[27–30] The rate of enol formation was determined by the rate of halogenation (or deuteration), and it has been established that the acid catalysed, slow enolization is followed by rapid halogen addition, consequently, the reaction has zero-order dependence on halogen concentration.[30–40] In addition, the observed rate cannot be higher than allowed by the rate of enolization. Although some authors[10,11,14,16] observed that permanganate oxidation of ketones does not meet these conditions, on the basis of the observation that the permanganate ion is particularly reactive to double bonds, the assumption that oxidation proceeds *via* the enol is still preferred.

In our investigations we arrived at the conclusion that being first order in permanganate concentration, the overall oxidation rate and the composition of intermediates (see later) cannot

$$-\frac{d[MnO_4^-]}{dt} = \frac{k_4k_3K_{H1}[H^+][S][MnO_4^-]}{k_{-3} + k_4[MnO_4^-]} \quad (2)$$

be in accordance with a mechanism based on enolization. By applying the enolization mechanism (in square brackets in Scheme 1) by means of steady-state approximation we would obtain eqn. (2). The rate constant for halogen addition on enol approaches the range of diffusion control,[41,42] therefore, in this case eqn. (2) is transformed into eqn. (3), where k_x is the rate constant of enolization measured by halogenation.

$$w = k_3K_{H1}[H^+][S] = k_x[H^+][S] \quad (3)$$

Eqn. (3) is not valid for permanganate oxidation, since first-order (not zero-order) dependence on $[MnO_4^-]$ is obtained, hence $k_{-3} \gg k_4[MnO_4^-]$. (Oxidation was found to be first-order in permanganate even at $[S] = 0.1$ and $[MnO_4^-] = 10^{-2}$ mol dm^{-3}.)

By estimation using eqn. (2) (and with the stipulation of $k_{-3} \gg k_4[MnO_4^-]$) at $[H^+] = 0.25$; $[S] = 10^{-2}$; $[MnO_4^-] = 10^{-3}$ mol dm^{-3} and by means of rate constants generally accepted in the literature: for acetone[30,40] $K_{H1}k_3 = 2.8 \times 10^{-5}$ dm^3 mol^{-1} s^{-1} and $k_{-3} = 6 \times 10^3$ s^{-1} (for butan-2-one[32] 5×10^{-5} dm^3 mol^{-1} s^{-1}

and 1.7×10^3 s^{-1}) we obtain: $-\mathrm{d}[\mathrm{MnO_4^-}]/\mathrm{d}t = k_4 K_{\mathrm{H1}}(k_3/k_{-3})[\mathrm{H^+}][\mathrm{S}][\mathrm{MnO_4^-}] = 1.25 \times 10^{-14}\, k_4$ (for butan-2-one $7.3 \times 10^{-14}\, k_4$). On the basis of the observed rate law [eqn. (1)] and the measured rate constants (Table 2) $-\mathrm{d}[\mathrm{MnO_4^-}]/\mathrm{d}t = 3.4 \times 10^{-8}$ mol dm^{-3} s^{-1} (for butan-2-one 4.4×10^{-8} mol dm^{-3} s^{-1}).

Comparison of the two values gives $k_4 = 3 \times 10^6$ dm^3 mol^{-1} s^{-1} (for butan-2-one 0.6×10^6 dm^3 mol^{-1} s^{-1}). Such high values, however, cannot be realistic, as in the permanganate oxidation of double bonds the magnitudes of the rate constants are in the range of 10^2–10^3 dm^3 mol^{-1} s^{-1} according to literature data.[25,43] Therefore, the enolization mechanism is highly improbable. (Incidentally, the condition $k_{-3} \gg k_4[\mathrm{MnO_4^-}]$ would not be valid at such a high k_4 value, therefore the reaction would not be first-order in $[\mathrm{MnO_4^-}]$.)

The permanganate ion is of ambiphilic nature, since the empty d-orbitals on the central metal are electrophilic whereas the electron-pairs on oxygen atoms are of nucleophilic character.[43,44] Ketones are reactive to nucleophilic addition, as their carbonyl C-atom is positively polarized, which is further enhanced by proton addition on the carbonyl O-atom. Consequently, acid catalysis suggests that the attack of the permanganate ion is not by electrophilic addition on the double bond of the enol, but it is nucleophilic addition on the carbon atom of the carbonyl group, resulting in an intermediate permanganate ester, as shown in Scheme 1. The rate of oxidation increases with decreasing ionic strength (Table 2), as expected for a reaction between ions with opposite charge. Protonation equilibria (K_{H1} and K_{H2}) are assumed to set in rapidly.[27,28,42] We consider two possibilities. According to the first approximation, oxidative decomposition of permanganate ester is the rate determining step. Obviously, K_{H1} is low and on the assumption that the reverse processes (k_{-1} and k_{-2}) in Scheme 1 are fast, steady-state approximation can be applied for [ester]. K_{H2} must be very high, since deprotonation of the alkoxy group is generally low (pK_a = 14–16[45] and in our definition $K_\mathrm{H} = 1/K_\mathrm{a}$). This leads to eqn. (4a), where E represents the intermediate permanganate ester.

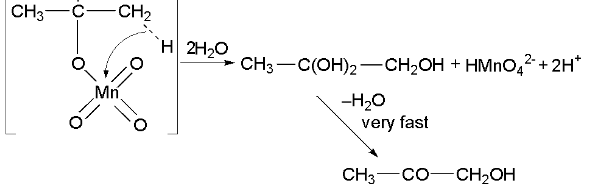
$$-\frac{\mathrm{d}[\mathrm{MnO_4^-}]}{\mathrm{d}t} = k[\mathrm{E}] = \left(\frac{kk_1 + kk_2K_{\mathrm{H1}}[\mathrm{H^+}]}{\frac{k_{-1}}{K_{\mathrm{H2}}[\mathrm{H^+}]} + k_{-2} + k}\right)[\mathrm{S}][\mathrm{MnO_4}] \approx \left(\frac{kk_1}{k_{-2}+k} + \frac{kk_2K_{\mathrm{H1}}[\mathrm{H^+}]}{k_{-2}+k}\right)[\mathrm{S}][\mathrm{MnO_4^-}] \tag{4a}$$

In the second approximation, the rate determining step is the formation of permanganate ester, the decomposition of which is then very fast. In this case the rate law given in eqn. (4b) is valid. As can be seen, both kinetic equations [eqn. (4a) and (4b)] are in agreement with the observed rate law, eqn. (1).

$$-\frac{\mathrm{d}[\mathrm{MnO_4^-}]}{\mathrm{d}t} = (k_1 + k_2K_{\mathrm{H1}}[\mathrm{H^+}])[\mathrm{S}][\mathrm{MnO_4^-}] \tag{4b}$$

In the case of butane-2,3-dione, significant hydration occurs.[46,47] In our earlier investigations,[1] we found that for acetaldehyde the hydrate form is more reactive to permanganate than the keto form, but separation into two individual rate constants does not seem to be possible. The situation must be similar for butane-2,3-dione.

For the activated complex (*e.g.* in the case of acetone) we propose the mechanism shown below. The oxidative decomposition of the ester may proceed by hydride ion abstraction or simple electron transfer simultaneously with proton elimination. This is also in agreement with the fact that for acetone $k_\mathrm{H}/k_\mathrm{D} = 5.1$.[16,48]



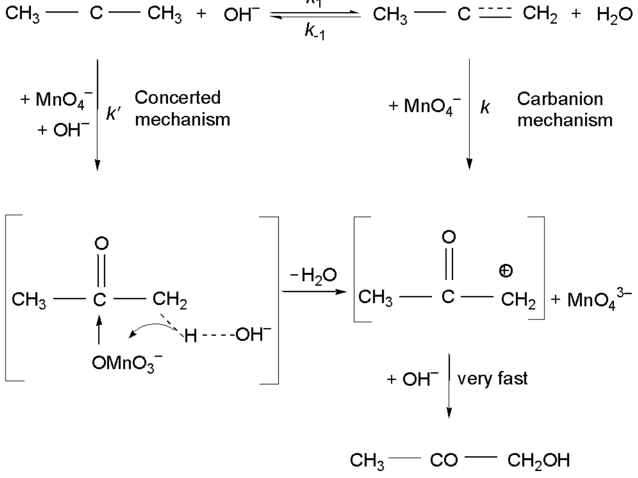
Oxidation proceeds *via* the following sequences: $\mathrm{CH_3{-}CO{-}CH_3} \longrightarrow \mathit{CH_3{-}CO{-}CH_2OH} \longrightarrow \mathrm{CH_3{-}CO{-}CHO} \longrightarrow \mathit{CH_3{-}CO{-}COOH} \longrightarrow \mathrm{CH_3{-}COOH + CO_2}$ and $\mathrm{CH_3{-}CO{-}CH_2{-}CH_3} \longrightarrow \mathit{CH_3{-}CO{-}CHOH{-}CH_3} \longrightarrow \mathit{CH_3{-}CO{-}CO{-}CH_3} \longrightarrow \mathrm{2\,CH_3{-}COOH}$.

In acetone oxidation, hydroxyacetone and pyruvic acid, in butan-2-one oxidation, acetoin and butane-2,3-dione could be detected by means of HPLC (italicized in the sequences). Acetic acid was formed as the end product in amounts of 1 and 2 mol, respectively, per 1 mol of reacted substrate. (We had previously found that in acidic media pyruvic acid is quantitatively oxidized to acetic acid by permanganate.[49]) The intermediates and the amount of end products support the mechanism proposed, since if the reaction proceeded *via* the enol, the formation of a hypomanganate diester followed by a fast chain rupture could be expected at the beginning of each sequence (see in square brackets in Scheme 1). The attack of permanganate ion cannot take place at the α-C-atom, as assumed by Sen *et al.*,[18] since in this case the methyl groups of pyruvic acid and butane-2,3-dione would not remain intact. The formation of permanganate ester must occur at the carbonyl C-atom (which is then followed by the scission of the loosened carbon–carbon bonds and not by proton elimination, at these two substrates; in accordance with this, we could not observe any kinetic isotope-effect ($k_\mathrm{H}/k_\mathrm{D} = 1.1$) for butane-2,3-dione).

Since the reaction proceeds in two-electron steps, the appearance of hypomanganate may be expected, though was, however, not detectable. This may be due to two reasons: either a very fast disproportionation,[42,50,51] or an extremely rapid reaction of hypomanganate, which has been observed in some cases.[52]

Alkali media

Permanganate oxidation of acetone was studied thoroughly by Wiberg and Geer[24] using alkali concentrations of 0.05–0.40 mol dm^{-3}. The mechanism was verified by means of kinetics and showed that permanganate ions reacted with enolate anions and not with enols, and direct electron abstraction occurred. It has also been established that the reaction is, not totally, only approximately first-order with respect to permanganate concentration. In the meantime, the rate constants of enolization, and thus, the rate of reverse reaction,[53] ($k_{-1} = 4.1 \times 10^4$ s^{-1} in Scheme 2) were measured. On the basis of this value it can be stated that the rate constant of direct oxidation (k) must be about 10^6–10^7 dm^3 mol^{-1} s^{-1}. If it were



Scheme 2

Table 3 Dependence of apparent second-order rate constants (k_B) on hydroxy ion concentration and the activation parameters

	k_B/dm^3 mol^{-1} s^{-1} [a]			
[OH$^-$]/mol dm^{-3}	Acetone	Hydroxyacetone	Butan-2-one	Butane-2,3-dione
0.05	5.8 (13)[c]	58	4.2	95
0.10	11 (21)	107	9.2	172
0.25	28 (53)	270	24	440
0.50	54 (109)	506	47	865
0.75	85 (154)	794	74	1320
1.00	111 (214)	1060	97	1780
0.10[b]	8.8	68	8.4	114
$\Delta H^‡$/kJ mol^{-1}	27.2	28	26.3	24.2
$\Delta S^‡$/J mol^{-1} K^{-1}	−125	−104	−129	−113

[a] [substrate] = 1.0×10^{-2} mol dm^{-3}; [MnO_4^-] = 1.0×10^{-3} mol dm^{-3}; I = 2.0 mol dm^{-3}; T = 25 °C. [b] Ionic strength 0.1 mol dm^{-3}. [c] In D_2O; I = 2.0 mol dm^{-3}.

lower we would find it strictly first-order, and if it were higher, it would be zero-order with respect to permanganate (as in the case of halogenation for the halogen). Although in a reaction between ions the rate constant may be as high as that (it is approximately in the range of a diffusion controlled process), this seems to be extremely high, especially in comparison with the oxidation constants of similar alkoxy anions,[54] which are lower than 10^3 dm^3 mol^{-1} s^{-1}.

Our current investigations were carried out at an alkali concentration higher than 0.05 mol dm^{-3} where permanganate is reduced only to manganate, which then reacts much slower. The reaction sequences (see below) point to two-electron steps, therefore a hypomanganate ion must be directly formed. Owing to its very fast reaction with permanganate (Mn(v) + Mn(vii) = 2 Mn(vi)) it does not accumulate, but due to this reaction a factor of two appears in the kinetic equations.

We found first-order kinetics for both hydroxy ion and for all four substrates studied (Table 3). The situation is somewhat different for permanganate, as under pseudo-first-order conditions the initial rates were not strictly proportional to the initial permanganate concentrations (Table 1).

Even at [OH^-] = 1 mol dm^{-3} the ratio of [enolate]/[keto] = 10^{-5} only, and less than 1% of enolate is present in enol form, as follows from literature data.[28,41,53,55–59] If the enolate ion is the reactive species then the kinetic eqn. (5) derived from the right

$$-\frac{d[MnO_4^-]}{dt} = 2k[\text{Enolate}][MnO_4^-] = \frac{2kk_1[MnO_4^-]}{k_{-1} + k[MnO_4^-]}[OH^-][S] \quad (5)$$

hand side of Scheme 2 (carbanion path) is valid (applying steady-state approximation for [enolate]).

If $k[MnO_4^-] \gg k_{-1}$ then the reaction must be zero-order in [MnO_4^-], and in this case the rate of permanganate consumption would be maximal. The rate of permanganate consumption measured at [S] = 0.1; [MnO_4^-] = 10^{-2} mol dm^{-3} considerably exceeded (by about eight times) this "maximal" rate (calculated with the highest literature values: k_1 = 0.220 dm^3 mol^{-1} s^{-1} for acetone[59] and 0.128 dm^3 mol^{-1} s^{-1} for butan-2-one[58]), but near first-order kinetics were found in [MnO_4^-] under such concentration conditions as well. This suggests the possibility of a further reaction path, that is, a concerted path with two reaction centres, which is shown on the left hand side of Scheme 2. The interaction between the permanganate ion and the electrophilic centre of the ketone promotes the abstraction of a proton by a hydroxy ion, *i.e.* the equilibrium k_1/k_{-1} will be shifted towards the enolate anion. This path may also explain the fact that nearly first-order dependence in [MnO_4^-] can be observed for different substrates (and hence, for different ratios of k_{-1} and k as well). For example, in the case of hydroxyacetone, zero-order kinetics in permanganate would be observed owing to the very low k_{-1} value (k_{-1} = 190 s^{-1}), however, this is not the case as can be seen in Table 1. For both paths the common kinetic law is given in eqn. (6) (k_B stands for measured rate constants given in Table 3).

$$-\frac{d[MnO_4^-]}{dt} = 2\left(k[MnO_4^-] + \frac{kk_1[MnO_4^-]}{k_{-1} + k[MnO_4^-]}\right)[OH^-][S] \approx k_B[S][MnO_4^-] \quad (6)$$

The dependence on ionic strength is rather low, but it still points to a reaction between particles with the same sign of charge, which is in accordance with both paths. The great negative entropy of activation is rather in agreement with the concerted path, which requires a greater increase in organization. Undeuterated acetone reacts with a rate constant about twice as high in D_2O as in H_2O (in parentheses in Table 3) as can be expected owing to the higher nucleophilicity[60] of DO^- compared to HO^-. This observation is in accordance with both paths.

The HPLC method was applied for the detection of intermediates (those detected qualitatively are italicized in the sequences): acetone, $\mathrm{CH_3{-}CO{-}CH_3} \longrightarrow \mathit{CH_3{-}CO{-}CH_2OH} \longrightarrow \mathrm{CH_3{-}CO{-}CHO} \longrightarrow \mathit{CH_3{-}CO{-}COOH} \longrightarrow 0.9\ \mathrm{(COOH)_2} + 0.1\ \mathrm{CH_3{-}COOH}$ and butan-2-one, $\mathrm{CH_3{-}CH_2{-}CO{-}CH_3} \longrightarrow \mathit{CH_3{-}CH_2{-}CO{-}CH_2OH} \longrightarrow \mathrm{CH_3{-}CH_2{-}CO{-}CHO} \longrightarrow \mathit{CH_3{-}CH_2{-}CO{-}COOH} \longrightarrow \mathit{CH_3{-}CHOH{-}CO{-}COOH} \longrightarrow \mathrm{CH_3{-}CO{-}CO{-}COOH}$.

Oxidative chain rupture of the latter may occur at different sites: path **A**: $\mathrm{CH_3{-}CO{-}CO{-}COOH} \longrightarrow \mathrm{(COOH)_2} + \mathrm{CH_3{-}COOH}$. path **B**: $\mathrm{CH_3{-}CO{-}CO{-}COOH} \longrightarrow \mathit{CH_3{-}CO{-}COOH} \longrightarrow 0.9\ \mathrm{(COOH)_2} + 0.1\ \mathrm{CH_3{-}COOH}$. Butane-2,3-dione, $\mathrm{CH_3{-}CO{-}CO{-}CH_3} \longrightarrow \mathit{CH_3{-}CO{-}CO{-}CH_2OH} \longrightarrow \mathrm{CH_3{-}CO{-}CO{-}CHO} \longrightarrow \mathrm{CH_3{-}CO{-}CO{-}COOH}$ (followed by paths **A** and **B** again).

No aldehydes could be observed in any of the four substrates, which may be due to the fact that no great accumulation of aldehydes can be expected owing to their high reactivity, and in addition, the method applied is very insensitive to aldehydes. The end products, acetic acid and oxalic acid, were determined with great accuracy by common analytical methods.

Both in the case of acetone and hydroxyacetone, the ratio oxalic acid : acetic acid = 9 : 1 is in agreement with our earlier experiments with pyruvic acid.[49] It should be noted that Wiberg and Geer[24] found acetic acid in higher amounts (this may be, however, due to the rather low conversion applied for analysis, in addition, we do not consider sulfite ion to be an appropriate quenching reagent). Other authors,[61–63] on the other hand, observed amounts very similar to us.

In the case of butane-2,3-dione and butan-2-one, 1 mmol substrate produced about 0.95 mmol oxalic acid independent of [OH^-], whereas the amount of acetic acid decreased from 0.90 mmol to 0.55 mmol when alkali concentration increased from 0.1 to 1.0 mol dm^{-3}. This is probably due to the different paths of oxidative decomposition of the common intermediate, 2,3-dioxobutyric acid. (With an increase in [OH^-] the originally predominant path **A** becomes suppressed.)

Conclusion

In conclusion, the following may be established. In acidic media oxidation cannot proceed *via* enolization, since neither the kinetics nor the composition of intermediates and end products is in agreement with this mechanism. Acid catalysis points to nucleophilic addition, and the decomposition of the permanganate ester formed is the rate determining step. The permanganate ester is formed on the carbonyl C-atom and not on the α-C-atom (which would be electrophilic substitution). This is also supported by the fact that if the carbonyl group is coupled to a loosened bond (as in pyruvic acid and butane-2,3-dione) rupture of the latter will occur, and the alkyl group will remain intact.

Oxidation starts at the same site of the molecule as halogenation, but later on various differences can be observed. In the case of butan-2-one both halogenation and oxidation begin at C-atom 3. Repeated formation of an enol double bond at the same site is hindered owing to the electron withdrawing effect of the halogen atom already present. Therefore, further halogenation is more likely to occur at the other site of the molecule (at the other methyl group for acetone and at the C-atom 1 for butan-2-one) with a simultaneous decrease in the reaction rate. In contrast to this, oxidation continues at the site where it had started, and with an increasing reaction rate (compare the k values of acetone and hydroxyacetone), since the O-atom further loosens the C–H bond on the same carbon atom. This phenomenon points to the difference between the two processes. It may also be established that in the case of a loosened C–H bond, proton elimination can be expected, which renders electron transfer more probable than hydride ion abstraction in the rate determining step.

In alkali media, in the enolate anion of butan-2-one the negative charge is destabilized at C-atom 3 by the positive inductive effect of the adjacent methyl group, therefore, the negative charge is localized at C-atom 1. Consequently, for both processes, the electrophilic attack of halogen and the electron abstraction by the permanganate ion, *i.e.* oxidation, take place at the same site of the molecule. This conclusion is valid for all ketones studied. Both reactions proceed further at the same site and with increasing reaction rate, for in the enolate anion–carbanion resonance hybrid system the electron is more probably localized at the site where an electronegative atom or atoms already exist. In accordance with this, although the two reactions are basically different, both take place at the same site on the molecule.

Experimental

Materials

The reagents $KMnO_4$, $NaClO_4$, $HClO_4$, and NaOH were of analytical grade (Merck). The substrates were of analytical grade (Fluka), purified by fractional distillation and dried with 4 Å molecular sieves. Hexadeuterated butane-2,3-dione was prepared by a method described in the literature.[64]

Kinetics

Kinetic measurements were carried out in a large excess of substrate under pseudo-first-order conditions. Ionic strength was maintained with $NaClO_4$. The concentration of [H^+] was adjusted with $HClO_4$ or with Britton–Robinson buffers, and pyrophosphate ions were added to avoid disproportionation and fast reactions of Mn^{3+}. Alkali concentration was adjusted with NaOH, and the stock solution of substrate did not contain any alkali to avoid aldol dimerization, which is slow relative to oxidation.[65,66]

Permanganate consumption was monitored with the use of a Hewlett-Packard spectrophotometer (8452A) coupled to a stopped-flow device (developed in our laboratory). The log ($A - A_\infty$) *vs.* time plots (A is the absorbance at 524 nm) showed a slight curvature owing to consecutive reactions of the intermediates formed in the oxidation. Therefore the rate constants were computed from the initial slopes of the plots determined by means of a Hewlett-Packard computer (9000–300) directly coupled to the spectrophotometer.

The order related to the [substrate] was determined at 0.25 M acid or base concentration with $[MnO_4^-]_0 = 1.0 \times 10^{-3}$ M, by varying substrate concentration between 1.0×10^{-2} and 10×10^{-2} M.

If the rate determining step is followed by very fast reactions where further MnO_4^- molecules are consumed, these reactions act as multipliers in the rate constant of the first reaction. In order to determine this kinetic factor (v) we applied the relatively sensitive method of reacting reagents in the presumed initial concentration ratio v. If this ratio is correct, then the integrated kinetic equation, $1/[MnO_4^-] - 1/[MnO_4^-]_0 = kt$, must be valid, and the k value gained from the slope must be equivalent to the k value gained under pseudo-first-order conditions. Although the $1/[MnO_4^-]$ *vs.* time plots always showed a curvature, the k values determined from the initial section of the plots verified the validity of $v = 1$ in acidic and $v = 2$ in alkali media.

The activation parameters were measured at 0.25 M acid or alkali concentrations between temperatures of 288 and 318 K.

Products

In order to determine the end products, we added a solution of 1.0×10^{-3} M substrate to a solution of 2.0×10^{-2} M permanganate. In acidic media pyrophosphate ion (3 × the concentration of permanganate) was also present. After the reaction was completed, the excess permanganate and Mn^{3+} or manganate formed were reduced with hydrazine hydrate to MnO_2, which was then filtered. Acetic acid was distilled from the solution after the addition of phosphoric acid (up to 25%) and then titrated. Oxalic acid was precipitated with calcium ions by the standard method.

For the determination of intermediates a reaction mixture containing the substrate in 1.0×10^{-2} and permanganate in 1.0×10^{-3} M initial concentrations was prepared. After quenching and filtering, the pH was adjusted to 2.75, and the mixture was diluted to 0.1 M ionic strength. Elution was carried out on a column filled with Nucleosil C_{18}, using an aqueous solution of KH_2PO_4 (0.1 M) containing 3.75×10^{-3} M tetrabutylammonium hydroxide (with pH adjusted to 2.75), as the eluent. Measurements were taken on an ISCO instrument (Model 2350, detector V4). Only qualitative measurements were made.

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