

Kinetics of the Oxidation of Acetoin with Cerium(IV)

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In earlier studies on the oxidation of hydroxylic compounds, we measured the rates of oxidation of eight monosaccharides with the lanthanoid cerium(IV).¹ It appeared that two complexes formed in each case. The first complex, formed during mixing in the stopped-flow apparatus, subsequently dissociated by Michaelis–Menten kinetics to a lesser extent to oxidation products but mainly to form a second, more stable complex.

Acetoin, MeCOCH(OH)Me, which has a secondary alcohol group, can be considered a model compound for aldoses ($C_{(1)}-C_{(2)}$ complexation and cleavage) and ketoses ($C_{(2)}-C_{(3)}$ complexation and cleavage). Glucose and mannose are oxidized to arabinose, whereas fructose is oxidized to erythrose.²

The eight monosaccharides studied¹ exist in aqueous solution mainly in pyranose and furanose ring forms and only in small amount in open-chain forms; all forms are in equilibrium during the oxidation because the rate of mutarotation is much faster than the rate of the oxidation.^{3,4} By contrast, acetoin exists solely in the open-chain form, and this difference was expected to give new information about the progress of the oxidation of monosaccharides.

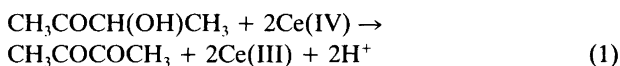
Experimental

Ceric ammonium nitrate (*purissimum*), Fluka AG) was dissolved in de-ionized water in a specially designed glass-stoppered flask,⁵ equipped with a side-arm with sintered-glass funnel. Hydrous ceric oxide (ceric hydroxide) was precipitated by the addition of ammonium hydroxide, and then washed with water and dissolved in aqueous HClO₄ to yield a stock solution of ceric perchlorate.

For the determination of the rate constants of the fast oxidation, ceric perchlorate in aqueous HClO₄ was mixed with acetoin in aqueous HClO₄ in a Gibson–Durrum type of stopped-flow apparatus. The solutions were in contact only with glass, stainless steel (type 304) and Teflon. The data acquired from the apparatus were registered with an on-line Datalab transient-recorder DL 902, visualized with an oscilloscope and analyzed with an on-line microcomputer programmed in BASIC to optimize the value of the pseudo-first-order rate constant.

A PU8700 UV/VIS spectrophotometer from Pye Unicam Ltd., programmed for rate measurements, was used for the determination of the rate constants of the slow oxidation.

The kinetic results indicate a reaction in which acetoin is oxidized to biacetyl as the first reaction product [eqn. (1)].



Biacetyl could not be isolated because it rapidly oxidizes to acetic acid as the final product. Its formation was nevertheless confirmed with the help of an automatic purge and trap concentrator/sample introduction system (Tekmar LSC 2000) connected to the GL/MS instrument (ITD, Perkin–Elmer). The oxidation of acetoin to biacetyl has previously been demonstrated in experiments where the oxidizing agent was V(V),⁶ Cu(II)⁷ and Fe(III).⁸

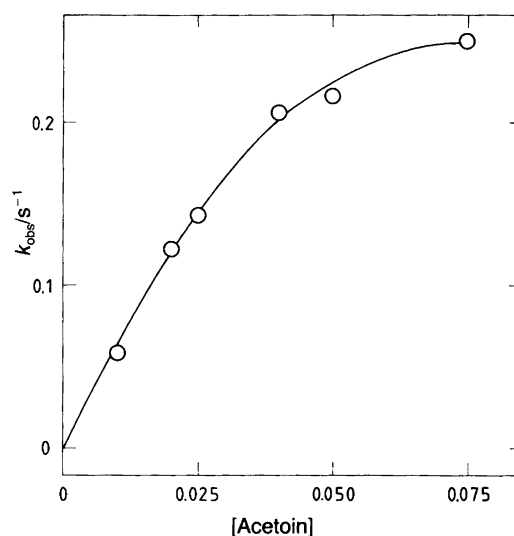


Fig. 1. Effect of acetoin concentration on the pseudo-first-order rate constant k_{obs} for the fast oxidation of acetoin with 3.50×10^{-3} M Ce(IV) in aqueous 1.000 M HClO₄ at 25°C.

Table 1. The estimated proportions of the open-chain forms of monosaccharides and kinetic data for the fast oxidation of monosaccharides and acetoin in water at 25 °C.

Compound	Proportion of the open-chain form		Kinetic data	
	from kinetics	from polarography	$k_{\text{diss}}/\text{s}^{-1}$	$K_{\text{ass}}/\text{M}^{-1}$
Glucose	0.040 ^a	0.024 ^b	0.72 ^c	34 ^c
Arabinose	0.26 ^a	0.28 ^b	3.3 ^c	67 ^c
Fructose	0.57 ^a	—	3.0 ^c	140 ^c
Acetoin	100	—	0.78 ^d	8.4 ^d

^aRef. 9, $[\text{HClO}_4] = 1.471 \text{ M}$. ^bRef. 10, at pH 7.0. ^cRef. 1, $[\text{HClO}_4] = 1.000 \text{ M}$. ^dThis work, $[\text{HClO}_4] = 1.000 \text{ M}$.

Results and discussion

As with the monosaccharides, two complexes formed in the oxidation. The first complex had an absorption maximum at 375 nm and this wavelength was used for the stopped-flow studies of the fast reaction. The results are given in Fig. 1. The shape of the curve (pseudo-first-order rate constant vs. [acetoin]) shows that the first-order rate in [acetoin] at low acetoin concentration approaches the zero-order rate in [acetoin] when the acetoin concentration increases so much that no more complex can form. The kinetics, in accordance with Michaelis–Menten kinetics, follow the linear eqn. (2).

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{diss}}K_{\text{ass}}} \times \frac{1}{[\text{acetoin}]} + \frac{1}{k_{\text{diss}}} \quad (2)$$

Experimentally we found that eqn. (3) holds, with a

$$\frac{1}{k_{\text{obs}}} = (1.53 \pm 0.09) \times 10^{-1} \frac{1}{[\text{acetoin}]} + (1.29 \pm 0.45) \quad (3)$$

correlation coefficient of 0.9935. From eqn. (3), the values 8.4 M⁻¹ for K_{ass} and 0.78 s⁻¹ for k_{diss} were obtained. The oxidation accounts for about 35 % of the dissociation and the formation of a second, more stable complex for about 65 %, as measured from the absorption of Ce(IV) at 280–320 nm before and after the fast reaction.

The low proportions of the open-chain forms of monosaccharides have been estimated from kinetic⁹ and polarographic¹⁰ data. Some illustrative data are collected in Table 1. The magnitudes of K_{ass} are seen to be of the same order for monosaccharides and acetoin. Thus the values of K_{ass} show that the ring forms of monosaccharides participate in the complex formation and suggest that this occurs more easily than the complex formation of open-chain acetoin. Because chelate complexes are more stable than acyclic species,¹¹ fast reactions of monosaccharides, taking glucose as an example, can be considered to involve both C₍₁₎ and C₍₂₎ hydroxy groups of α-D-glucopyranose in a chelate complex.¹ This complex disproportionates to an extent of 8.5 % to form a radical which is rapidly oxidized to arabinose.^{1,2,11}

The oxidation of the second, more stable complex was studied by conventional spectrophotometry at 339 nm where neither acetoin nor the final product absorb. An example of the time dependence of absorbance for this reaction is seen in Fig. 2. The results are collected in Table 2. At low [acetoin], the order with respect to [acetoin] is a half but it decreases to zero with increasing [acetoin].

As the formation of the second complex has not, to our knowledge, been reported for Ce(IV) oxidations of other compounds except monosaccharides,¹ the behavior must arise not from Ce(IV) itself but from the vicinal carbonyl–alcohol grouping. The first complex is probably stabilized by another acetoin molecule to form the second complex, which in a rate-determining pre-equilibrium step forms a reactive species which is then rapidly oxidized by Ce(IV).

Table 2. The slow oxidation of acetoin in water at 25 °C. $[\text{Ce(IV)}] = 3.60 \times 10^{-3} \text{ M}$, $[\text{HClO}_4] = 1.000 \text{ M}$.

[Acetoin]/M	$(d[\text{Ce(IV)}]/dt)/\text{mol dm}^{-3} \text{ s}^{-1} \text{ }^a$	$(d[\text{Ce(IV)}] \times [\text{Acetoin}]^{-1/2})/\text{mol}^{1/2} \text{ dm}^{-3/2} \text{ s}^{-1} \text{ }^a$
0.0101	1.80×10^{-3}	0.0180
0.0305	3.05×10^{-3}	0.0175
0.0610	4.25×10^{-3}	0.0172
0.0997	4.33×10^{-3}	0.0137
0.203	4.15×10^{-3}	0.0092

^aThe slopes of the linear part. See Fig. 2.

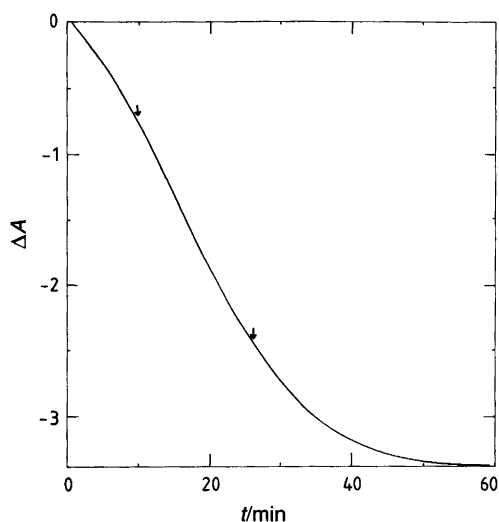
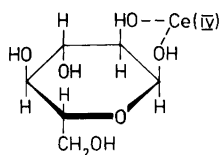


Fig. 2. Absorbance of Ce(IV) vs. time for the slow oxidation of 1.01×10^{-2} M acetoin with 3.60×10^{-3} M Ce(IV) in aqueous 1.000 M HClO₄. See Table 2.



Gupta *et al.*¹² have recently reported a pseudo-zero-order rate in the oxidation of D-fructose with dodecatungstocobaltate(III). The interpretation offered involves the rate-determining acid-catalyzed enolization of fructose, followed by the fast reaction of the enediol with Co(III) to give the products.

It is noteworthy that the oxidation of monosaccharides with the lanthanoid cerium(IV) differs dramatically from that with another one-electron oxidant, i.e. the transition metal ion vanadium(V). With vanadium(V) the reaction occurs with the open-chain monosaccharide.^{9,13} The ratio of the rate constants $k_2(\text{acetoin})/k_2(\text{glucose})$, for example, is 2500 for V(V) oxidation, whereas the Ce(IV) complexes of acetoin and glucose dissociate at approximately the same rate (Table 1).

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