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A soluble Manganese(IV) Intermediate in the Permanganate Oxidation of Uracils

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The permanganate oxidation of alkenes is generally believed to occur via an intermediate cyclic hypomanganate ester both in alkaline [1, 2] and acidic media [3–5]. Two types of intermediates have been detected in these reactions, *viz.* manganese(III) [4–7], and a yellow-brown species [8–11] best recognized by a transient maximum on the 420 nm stopped-flow trace. The latter intermediate was in several cases regarded as the long-sought but elusive hypomanganate ester invariably postulated in the permanganate oxidation of olefins and acetylenes. It has been recently shown that the 420 nm intermediate observed with *trans*-cinnamic acid [12] is in fact a soluble manganese(IV) species.

We now report four additional cases in which the 420 nm intermediate turns out to be a manganese(IV) compound. The uracil derivatives listed in Table I were oxidized with permanganate ion in phosphate buffered solutions of pH 6.7. The reactions were followed by repetitive scanning of the uv–vis region using a Beckman ACTA MIV spectrophotometer and/or by recording the absorbance *vs.* time curves at preselected wavelengths. A series of such spectra is shown in Figure 1 for 6-methyluracil. In agreement with earlier findings [10], the absorbance at 420 nm first increases, then reaches a stable value persisting for several hours. The isosbestic point at 469 nm implies one reactant (MnO_4^-) and one product,

TABLE I. Average Oxidation State of Manganese in the 420 nm Intermediate[a].

Compound	Oxidation State	Time Elapsed, min
Uracil	3.60	4.0
	3.57	5.0
	3.47	6.0
	3.43	15.0
6-Methyluracil	3.75	110.0[b]
	3.77	120.0
	3.70	120.0[c]
5-Methyluracil	3.39	1.0
	3.40	1.5
	3.40	2.0
	3.35	5.0
5-Fluorouracil	3.33	1.0

[a] 4×10^{-3} *M* compound; 8×10^{-4} *M* MnO_4^-; T = 25 °C, phosphate buffer, pH 6.70. [b] 4×10^{-4} *M* MnO_4^-. [c] 4×10^{-5} *M* MnO_4^-.

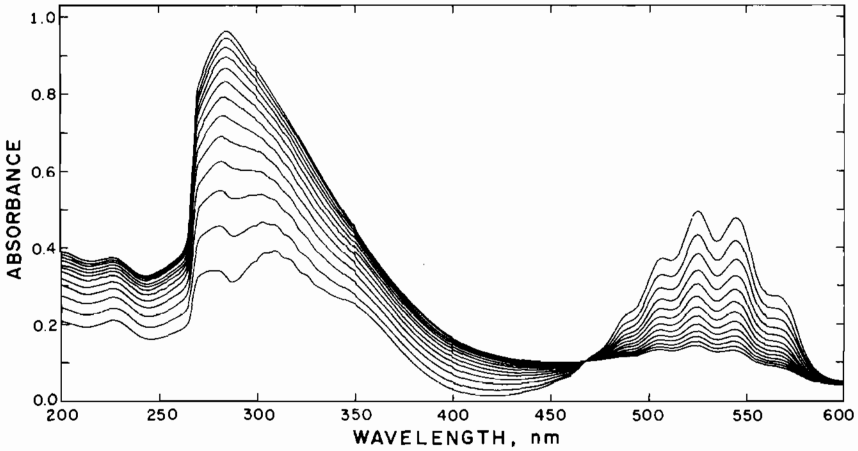

Figure 1. Successive uv–vis spectra (at 5.5 min intervals) for the reaction of 4×10^{-3} *M* 6-methyluracil with 4×10^{-4} *M* MnO_4^- in a phosphate buffered aqueous solution of pH 6.7 at 25 °C (0.5 cm cells; reference cell contains 3.6×10^{-3} *M* 6-methyluracil in same buffer).

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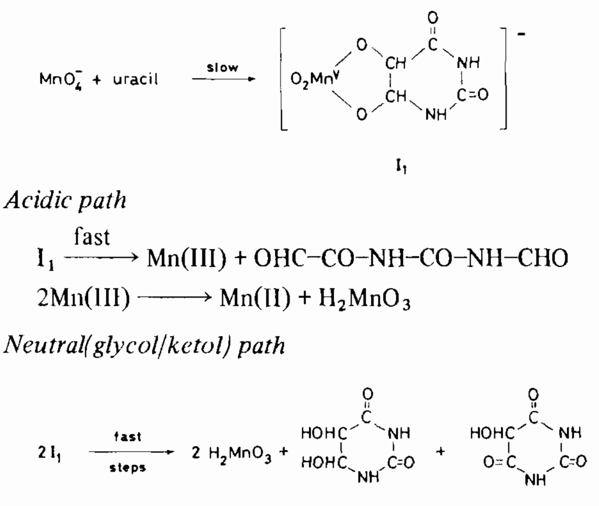
absorbing in the visible region. The latter is the 420 nm intermediate, which has an unusually long lifetime under these conditions. The reaction is accompanied by the increase of a band at 330 nm, which initially shows the structure of the MnO_4^- band at 309–325 nm. With the progress of the reaction, the 330 nm band loses its structure as MnO_4^- gradually disappears. Faster but otherwise identical spectral changes have been observed with the other uracil derivatives listed in Table I. In the case of uracil itself, the 420 nm intermediate is less stable, its rate of disappearance being comparable with that of its formation.

The oxidation state of manganese in the 420 nm intermediate has been determined by quenching the solutions with excess NaI and titrating the iodine released against standard thiosulfate. The acidic NaI solution was added to the reacting mixture after the absorbance at 420 nm had reached its stable value, *i.e.* after the complete disappearance of MnO_4^-. In the case of uracil, this was done at the time of maximum absorbance at 420 nm. The results of the quenching experiments are shown in Table I as the average oxidation state of manganese after full conversion of the added MnO_4^- to the 420 nm intermediate.

It is clear from the results that in all four cases the average oxidation state of manganese is +3.50 ± 0.13. This is obviously inconsistent with a stable manganese(V) intermediate. We propose that the yellow-brown substance, *i.e.* the 420 nm intermediate, is a *soluble manganese(IV)* species probably identical with that observed in the permanganate ion oxidation of *trans*-cinnamic acid [8, 12]. The non-integer value of the average oxidation state is due to the contribution of a path producing manganese(IV) via the disproportionation of manganese(III). The latter is known to form in acidic media; this path is apparently not fully suppressed at pH 6.7 used in the present work. The observed behavior can be rationalized in terms of Scheme 1.



Acidic path

$$I_1 \xrightarrow{\text{fast}} \text{Mn(III)} + \text{OHC–CO–NH–CO–NH–CHO}$$

$$2\text{Mn(III)} \longrightarrow \text{Mn(II)} + H_2MnO_3$$

Neutral(glycol/ketol) path

Scheme 1.

Attack of the permanganate ion on the uracil derivative leads to the formation of an undetectable hypomanganate intermediate (I_1), which rapidly decomposes in two ways. The acidic path yields manganese(III) and, upon disproportionation, 0.5 mol manganese(IV) per mol MnO_4^- consumed (in view of the lack of information on the composition of this soluble manganese(IV) species, we regard it as H_2MnO_3, one of several possibilities, *e.g.* phosphate complexes). The neutral path yields an equimolar mixture of the corresponding glycol and ketol (similarly to other olefins [15]), as well as 1 mol manganese(IV) per mol MnO_4^- consumed. Depending on the relative contribution of these two routes, the amount of the soluble manganese(IV) species may vary between 0.5 and 1.0 mol per mol MnO_4^- added. This corresponds to 20–40% of the oxidation power of MnO_4^-, *i.e.* to an average oxidation state between +3 and +4. Apparently, both routes contribute to the same extent, which explains the observed oxidation state of +3.50. As H_2MnO_3 disappears without the precipitation of MnO_2, it should oxidize the organic reactant or intermediate(s). These reactions have not been investigated.

The transient appearance of the 420 nm species has been detected in the permanganate oxidation of *cis*-2-butene-1,4-diol [13], diethyl maleate and fumarate [14], crotonic acid [7] and some chloro- and bromomaleic acids [5] in acidic solutions. In these cases too the 420 nm intermediate has been shown to be a soluble manganese(IV) compound formed via the disproportionation of its manganese(III) precursor.

The results reported here should not be regarded as evidence against the intermediacy of manganese(V) in permanganate oxidations of unsaturated compounds. However, the short lifetimes of hypomanganate species do not permit their detection by the techniques available at present. It seems likely that the formation of relatively stable, soluble manganese(IV) intermediates is encountered more often than expected and this possibility should be checked whenever oxidation states are assigned to transient manganese species.

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