Notes

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On the Free Radical Intermediates formed during the
Oxidation of L-Ascorbic Acid

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In the foregoing paper,²⁾ an ESR evidence was put forward that at least two types of radicals, denoted as *l*- and *m*-species, are formed during the oxidation of L-ascorbic acid with Ti^{3+} - H_2O_2 in a continuously flowing reaction system. Further works were carried out, using a similar technique and under almost the same reaction condition, to examine whether such radical species are formed also during the oxidation of L-ascorbic acid with the other oxidizing agents such as the Fenton reagent. In Table I are shown the oxidizing agents investigated and the type of radicals formed together with the result of the earlier work.²⁾

As shown in Table I, the *m*-species were not observable except for the Ti^{3+} - H_2O_2 or Ti^{3+} -EDTA- H_2O_2 system; only *l*-species were detectable in most cases.

TABLE I. Type and Intensity of ESR Spectra, *l* and *m*, observable during the Oxidation of L-Ascorbic Acid

Oxidizing agent	Type and relative intensity of ESR spectra	
	<i>l</i>	<i>m</i>
Ti^{3+} -(EDTA)- H_2O_2	++	++
Fe^{3+} - H_2O_2	+	—
Fe^{3+} -EDTA- H_2O_2	++	—
VO^{2+} - H_2O_2	+	—
Ce^{4+}	++	—
Ce^{4+} - H_2O_2	+	—
K_2CrO_4	+	—
KMnO_4	+	—

Norman, *et al.*³⁾ showed, studying the oxidation of organic compounds with hydrogen peroxide and various metal ions by a rapid-mixing flow technique, that difference in the ESR spectra observable between the Ti^{3+} - H_2O_2 and Fe^{2+} - H_2O_2 systems could be attributable to different oxidizing ability of Ti^{4+} and Fe^{3+} ions produced by the reactions of Ti^{3+} and Fe^{2+} with H_2O_2 .

In order to ascertain their suggestion and also to clarify the difference in the reactivity between metal ions such as Ce^{4+} and OH radicals involved in the Ti^{3+} - H_2O_2 or Fe^{2+} - H_2O_2 system, the following experiments were carried out by means of a T-shaped flow-cell after Norman, *et al.*³⁾ This type of cell enables us to add the third reactant shortly after the other two reactants have been mixed and before the solution reaches the spectrometer cavity.

Both *l*- and *m*-spectra were observed, as described previously,²⁾ when none of the third reactant was introduced. Then, when 0.001 M Fe^{3+} solution, as the third reactant, was in-

1) Location; Hongo 7-3-1, Bunkyo-ku, Tokyo.

2) Y. Kirino and T. Kwan, *Chem. Pharm. Bull.* (Tokyo), **19**, 718 (1971).3) R.O.C. Norman and P.R. West, *J. Chem. Soc. (B)*, **1969**, 389.

troduced at the second mixing point, only *m* disappeared specifically. In the first place, this phenomenon may eliminate the possibility of the consecutive reaction, $m \rightarrow l$, because *l* should also disappear if the species were to be produced from *m*. Secondly, it indicates that even if both *l*- and *m*-species were generated during the oxidation with Fe^{2+} - H_2O_2 , *m*-species could not necessarily be detectable because of its short lifetime caused by the rapid oxidation by the Fe^{3+} ion formed. In the case of the Ti^{3+} - H_2O_2 oxidation, *m* could be alive, because of the lower oxidation potential of Ti^{4+} ion (*ca.* 0.05 V⁴⁾) as compared with Fe^{3+} (0.771 V⁵⁾).

On the contrary, specific disappearance of *m*-species was not observable when a Ce^{4+} solution (0.001, 0.005 M) was introduced at the second mixing point into the admixed solution of Ti^{3+} , H_2O_2 and L-ascorbic acid; both *l*- and *m*-species remained to be unchanged. The oxidation potential of Ce^{4+} is known to be as high as 1.61 V⁵⁾ and so Ce^{4+} may well be expected to oxidize at least *m*-species as Fe^{3+} has been presumed to do so. This was not actually the case. Therefore, the simple redox mechanism that Fe^{3+} oxidizes the *m*-species is still unsettled.

The *l*-species are quite stable and readily producible with a number of oxidizing agents while the *m*-species are not. The latter species may not be detected, even if produced, because of its short life-time or of absence.

Experimental

Acidified (0.1M H_2SO_4) solutions of 0.005M Ti^{3+} containing L-ascorbic acid (0.02 M) and of 0.1 M H_2O_2 were mixed at the first mixing point, and Fe^{3+} or Ce^{4+} solution, as the third reactant, was introduced at the second mixing point. Usual experimental conditions were as follows: The flow rates of Ti^{3+} , H_2O_2 , and the third reactant solutions were 40, 40 and 30 ml/min, respectively, and the time interval between the first and second mixing was 6 msec, and between the second mixing and the ESR cavity was 9 msec.

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- 5) W.M. Latimer, "Oxidation Potentials," 2nd. ed. Prentice-Hall, 1952.

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Synthesis of 1-Substituted-1,2,5,6-tetrahydro-4H-pyrrolo(3,2,1-*ij*) quinolin-2-one

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There is considerable literature dealing with the ring closure reaction *via* intramolecular nucleophilic addition to aryne intermediate. Pioneering work has been done by Huisgen²⁾ and by Bunnett.³⁾ Bunnett and his co-workers^{4,5)} reported the cyclization forming oxindole

- 1) Location: Aobayama, Sendai.
- 2) R. Huisgen and H. König, *Angew. Chem.*, **69**, 268 (1957).
- 3) B.F. Hrutford and J.F. Bunnett, *J. Am. Chem. Soc.*, **80**, 2021 (1958).
- 4) J.F. Bunnett and B.F. Hrutford, *J. Am. Chem. Soc.*, **83**, 1691 (1961).
- 5) J.F. Bunnett, T. Kato, R.R. Flynn and J.A. Skorcz, *J. Org. Chem.*, **28**, 1 (1963).