Notes

[Chem. Pharm. Bull. 19(4) 831—832 (1971)]

UDC 547.475.2.04 : 541.515

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

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(Received August 31, 1970)

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 *l*	*m*
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-

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[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 V[4]) as compared with Fe^{3+}(0.771 V[5]).

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 V[5] and so Ce^{4+} may well be expected to oxidize at leat *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.

Acknowledgement The authors wish to thank Takeda Chemical Industries, Inc. for generous supply of the pure sample of L-ascorbic acid.

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

Chem. Pharm. Bull.
19(4) 832—836 (1971)

UDC 547.832.07 : 547.759.07

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

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(Received September 17, 1970)

There is considerable litrature dealing with the ring closure reaction *via* intramolecular nucleophilic addition to aryne intermediate. Pioneering work has been done by Huisgen[2] and by Bunnett.[3] Bunnett and his co-workers[4,5] reported the cyclization forming oxindole

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[1] Location: *Aobayama, Sendai.*

[2] R. Huisgen and H. König, *Anegew. Chem.*, **69**, 268 (1957).

[3] B.F. Hrutfiord and J.F. Bunnett, *J. Am. Chem. Soc.*, **80**, 2021 (1958).

[4] J.F. Bunnett and B.F. Hrutfiord, *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).