Tetrahedron Letters No.57, pp. 5005-5008, 1969. Pergamon Press. Printed in Great Britain.

FREE RADICALS FORMED IN THE REACTION OF L-ASCORBIC ACID WITH HYDRAZINES

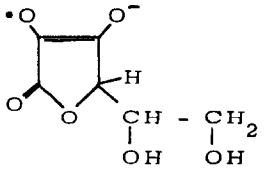
L. Burlamacchi, P. Sarti-Fantoni, E. Tiezzi

Istituto di Chimica Fisica, Istituto di Chimica Organica

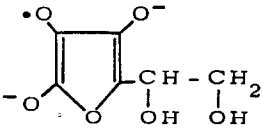
della Università di Firenze (Italia)

(Received in UK 29 October 1969; accepted for publication 11 November 1969)

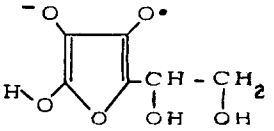
EPR studies have been reported on the formation of a free radical in the auto-oxidation of l-ascorbic acid for which structures I, II, III were postulated on the basis of the EPR spectra (1,2):



I



II



III

Hydrazine radical ions have been produced either during the oxidation of hydrazine by ceric ion (3) ($N_2H_4^+$ was formed) or during the electrode reactions in aqueous solutions (4).

In this letter the EPR spectra of free radicals, formed during the reaction of l-ascorbic acid with hydrazine and substituted hydrazines, are reported.

EPR spectra were registered with a Varian V-4502 X-band spectrometer.

Aqueous solutions of l-ascorbic acid were prepared to which hydrazine was added. The pH was varied by means of different relative concentrations of ascorbic acid and hydrazine. A color change was noted passing through bright orange to purple upon adding an oxidant (ceric ion; nitrite etc.) or upon leaving the solutions in air for 8 to 20 hours or more (sometimes for a few days). In the orange colored solution a paramagnetic species was detected which subsequently decomposed according to first order kinetics. The EPR signal disappeared when the colour of the solution became purple. The maximum concentration of the free radical was observed at pH=8.6. Both oxidation and temperature increase were found to enhance the concentration of the paramagnetic species.

In the conditions used for the preparation of the free radical, a white solid product (m.p. = 242°C) was obtained and recognized (I.R.) to be the oxalic dihydrazide.

The free radical EPR spectrum, is shown in fig.1. A g-value of 2,0044 and a

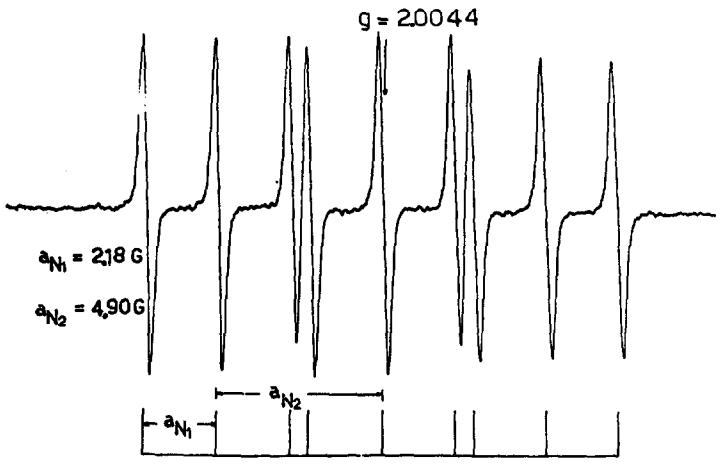


Fig.1 EPR Spectrum of hydrazine-l-ascorbic acid free radical.

linewidth ΔH = 0.33 G were measured. The spectrum presents isotropic hyperfine interaction with two different nuclei, both with spin I=1, i.e. the hydrazine nitrogens. The values of the nuclear hyperfine coupling constants are $a_{N_1} = 2.18 \pm 0.04$G and $a_{N_2} = 4.90 \pm 0.04$G.

The unusually high ratio ($a_{N_2}/a_{N_1} = 2.24$) between the two nitrogen splittings allows a complete resolution of the spectrum into three triplets.

The free radicals formed during the reaction between l-ascorbic acid and substituted hydrazines were obtained under the same experimental conditions reported for hydrazine. The formation of free radicals was noted to proceed more slowly. Fig.2 refers to N-methyl hydrazine. The spectrum consists of nine quartets (relative intensitites: 1:3:3:1) due to the splitting of the nitrogen hyperfine components by three equivalent hydrogen nuclei from the methyl group, although overlapping of nearly coincident lines gives rise to patterns 1;4:6:4:1 for the third-fourth and the sixth-seventh quartets. The isotropic coupling constants is $a_H = 0.45$ Gauss.

The nitrogen coupling constants are exactly the same as in the hydrazine case. N,N-dimethyl hydrazine gives the same hyperfine pattern as N-methyl hydrazine in spite of the presence of two methyl groups. The spectrum of the radical obtained by action of semicarbazide on l-ascorbic acid (Fig.3) has the same pattern as that of hydrazine radical, although the nine lines are not as well resolved.

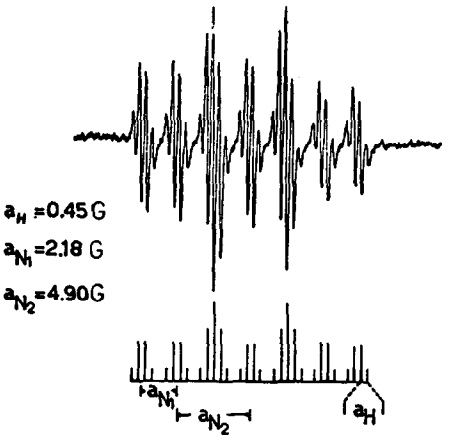


Fig.2 EPR spectrum of N-methyl-hydrazine-l-ascorbic acid free radical.

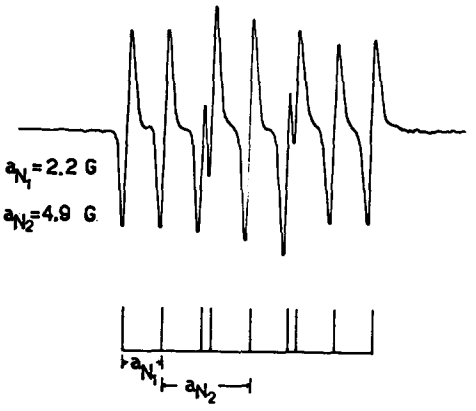
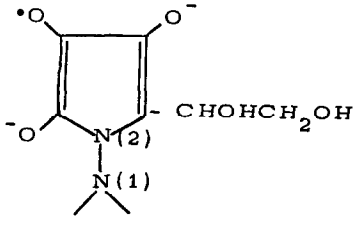


Fig.3 EPR spectrum of semicarbazide--l-ascorbic acid free radical.

The detection of the hyperfine structure due to the hydrazine protons failed in all cases in spite of several attempts under various experimental conditions, i.e. by using different solvents and different temperatures.

If the furan structure proposed for ascorbic acid radical is assumed (2) one may suggest that the radicals have the form:



This may be obtained by the attack of hydrazines on the ring of ascorbic acid followed

by ring closing to pyrrole derivatives via H_2O elimination. However a lack of detection of hydrazine protons hyperfine splitting does not allow an unambiguous assignment of the radical structure.

In order to explain the methyl protons hyperfine coupling a long range interaction via spatial overlapping between the quinoidal oxygen and the methyl group can be taken into account.

The interaction with only one methyl group in the N-N-dimethyl hydrazine radical is probably correlated with a steric hindrance of the side chain on the $N(CH_3)_2$ group.

References

1) C.Lagercrantz, Acta Chem.Scand., 18, 562 (1964) and references reported there in.

2) G.A.Russel et al.; Rec.Chem.Prog. , 27, 3 (1966).

3) J.Q.Adams and J.R.Thomas, J.Chem.Phys.,39, 1904 (1963).

4) S.Szpak, P.Stonehart and T.Katan, Electrochimica Acta, 10 563 (1965).

Acknowledgements

This research was supported by the Italian National Research Council (CNR).