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MONODEHYDRO-5,5'-IMINODIBARBITURIC ACID, A RADICAL PRODUCED BY THE REDUCTION OF MUREXIDE

Tadao KURATA and Masao FUJIMAKI
Department of Agricultural Chemistry, Faculty of Agriculture,
The University of Tokyo, Bunkyō-ku, Tokyo 113

The reduction of murexide with some reducing reagents such as L-cysteine (CySH) gave a stable radical product which was considered to be monodehydro-5,5'-iminodibarbituric acid from the results of ESR spectroscopy.

Murexide, 5,5'-nitrilodibarbituric acid monoammonium salt has been used as an indicator in complexometric titrations,1) and its spectral changes were discussed in terms of the detailed structures of the complexes with metal cations.2) However, little is known about the radical species produced by the reduction of murexide.

Recently, it was demonstrated that one of the radical species produced by the reaction of dehydro-L-ascorbic acid with α-amino acid was monodehydro-2,2'-iminodi-2(2')-deoxy-L-ascorbic acid (MDIDA)3) which was easily formed by the reduction of the red pigment, 2,2'-nitrilodi-2(2')-deoxy-L-ascorbic acid monoammonium salt (NDA)4) with some reducing reagents such as CySH. Since murexide has the same type of chromophoric system as that of NDA, production of the same kind of radical species by the reduction of murexide was also expected.

Sample solutions for ESR spectroscopy were prepared as follows: Several milligrams of murexide were dissolved in a small volume of dimethyl sulfoxide, and to this murexide solution was added a few drops of an aqueous solution containing a reductant such as CySH or L-ascorbic acid (ASA). On addition of these reducing substances, the purple color of the murexide solution gradually faded and finally disappeared completely. ESR spectra of a radical species which was produced during this color extinction were recorded with a JES-3BX spectrometer at room temperature.

Fig. 1 shows the ESR spectra of the radical produced by the reduction of murexide with CySH, and quite identical spectra were also obtained when the reduction was carried out with ASA. As shown in the schematic diagram given above Fig. 1-(A), the spectrum of the radical indicated the interaction of an unpaired electron with one nitrogen nucleus and one proton. When the radical was produced in the presence of deuterium oxide, however, its ESR spectrum [Fig. 1-(B)] which gave rather complex signal patterns due to the presence of undeuterated compound, indicated that the proton was replaced by a deuterium atom, and the deuterium coupling constant (1.1 G) was very close to the value expected from a_H=7.11 G after allowance for the difference in nuclear magnetic moment and spin.[5)] The high-field lines corresponding to transition between states for which the nitrogen nuclear spin quantum number $m_I(N)$ was -1 were much smaller and somewhat wider than the others. The same phenomenon is also observed in the spectra of MDIDA[3)] or in many other cases.[6)]

From the results described above, the structure of the radical was considered to be monodehydro-5,5'-iminodibarbituric acid [Fig. 1-(D)], and it was also suggested that the interactions of an odd electron with ring nitrogen nuclei and protons on them were very small or almost negligible. The spin density on the nitrogen may be estimated to be about 0.2 by using the simplified form of Karplus and Fraenkel equation.[7)] However, more elaborate studies are needed to discuss the detailed structure of the radical.

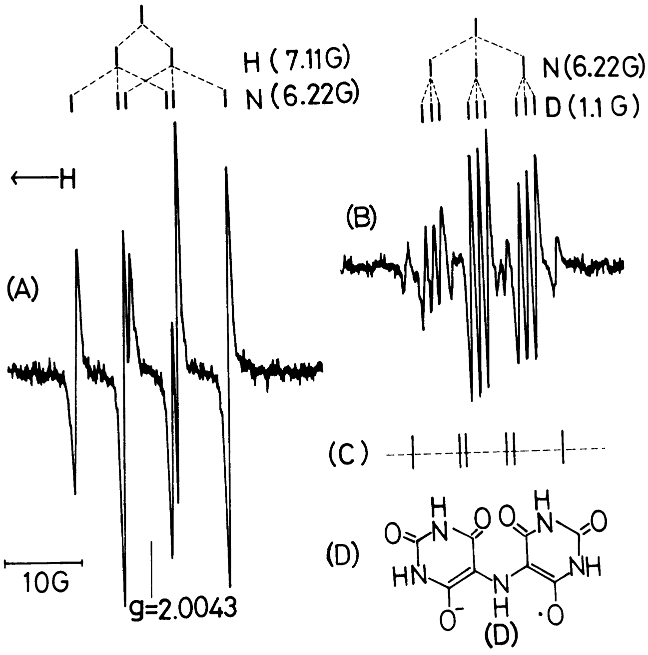

Fig.1 ESR spectra of the free radical produced by the reduction of murexide with CySH

(A): in H_2O

(B): in D_2O

(C): Signal positions of undeuterated radical

(D): Monodehydro-5,5'-iminodibarbituric acid

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