EPR OF RADICALS OBTAINED BY ANNEALING OF SINGLE CRYSTALS OF CYANIDE-DOPED KCl

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In the present work we studied one radical formed by irradiation at 77 K. We suggest that the EPR spectra arise from one radical ion that contains C,N and other atoms not identified.

EXPERIMENTAL

A single crystal of KCl doped with KCN that was 90% enriched with the isotope ^{13}C, was grown from the melt. The crystals were grown in air and the presence of oxygen during the growth process resulted in the formation of oxygenated free radicals which were absent in anaerobically grown specimens. The crystals were irradiated at 77 K with ultraviolet light, using high-pressure mercury lamps, Osram HBO of 500 W. The irradiation time was varied between 2 and 4 hours. The EPR spectrum was taken with an X-band EPR spectrometer. The microwave generator was a V-265 reflex klystron and the magnetic field was produced by a Varian 12-in. magnet.

RESULTS AND CONCLUSIONS

The EPR isotropic spectrum at 77 K is composed of two quintuplets and four triplets in a region of magnetic field different than that for the quintuplets. At a temperature of 179 K the quintuplets dissappear while the triplets present a large increase in intensity. In the region of magnetic field occupied by the quintuplets at 77 K there appear two more triplets. Thus as shown in Fig.1 the spectrum of EPR at 77 K is composed of the six triplets originating from the same paramagnetic center.

The origin of this spectrum was established attributing the splitting of triplets in two groups as due to the hyperfine interaction with the nuclei ^{13}C of nuclear spin $I=\frac{1}{2}$ with a relatively large isotropic hyperfine coupling constante A_0^C. The splitting of the triplets is due to the hyperfine interaction with two non-equivalent nuclei of N with nuclear spin I=1 with isotropic coupling constants A_0^{N1} and A_0^{N2}.

The radical ion EPR spectrum exhibit the following Hamiltonian parameters at 77 K

$$g_o = 2.0025, \qquad A_0^C = 142.3G,$$

$$A_0^{N1} = 38.3G, \qquad A_0^{N2} = 7.0G.$$

By annealing experiments the radical ion was observed to be stable below 236 K. The isotropic EPR spectrum disappeared and another isotropic spectrum appeared above 236 K(1).

The spectrum in Fig.1 is attributed to a single radical ion that contains in its structure C, two non-equivalent N and other unidentified atoms. We studied the effect of irradiation at temperatures between 77 K and 195 K and we noted that the effect is to produce atoms of N by the photolytic dissociation of the molecular impurities that contain this element(2). These atoms very probably are captured by substitutional ions of CNO^- or by CN^-, forming the paramagnetic radicals in study.

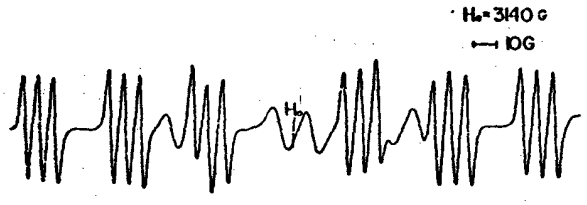

Fig.1 EPR spectrum of the radical ion at 77 K after irradiation at 77 K and annealing until 236 K

1. J.E.RODAS DURAN ET AL., J.Magn.Reson. 46,374 (1982).
2. J.E.RODAS DURAN and H.PANEPUCCI, in Bull.Magn. Reson.(1986).