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# ESR STUDIES OF γ-IRRADIATED SOLID CYCLOPENTANONE

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The γ-irradiated 3,3,4,4-cyclopentanone-$d_4$ was studied at low temperatures by means of ESR. The analysis of spectra and INDO calculations have indicated the presence of the anion radical.

In the course of studying the radiolysis of cyclopentanone[1], we became interested in trapping the possible reaction intermediate at low temperatures[2]. The 3,3,4,4-cyclopentanone-$d_4$ has been chosen for elucidating the ESR spectra. This compound was synthesized by an exchange reaction of the perdeutero compound with $H_2C$[3]. Analyses by a mass spectrometer and an infrared spectrometer have shown that over 95% of α-deterium is replaced by protium. The degassed samples were irradiated by $^{60}Co$ γ-rays with dose rate of $5.2 \times 10^5$ r $hr^{-1}$ for 3.5 hours at -196°C. ESR spectra were observed with a Varian E-4 spectrometer.

A broad spectrum obtained at -180°C in Fig. 1a changed into narrow quintet lines at -120°C in Fig. 1b with hyperfine coupling constant of 28 gauss, superimposed on rather broad lines. After corrections of spectrum by subtracting from it the spectrum of cell and the one still existing at -60°C, relative intensity of the quintet lines could be regarded as 1 : 4 : 6 : 4 : 1. These can be attributed to the anion radical with rather localized spin density on carbonyl group, four equivalent α-protons giving the hyperfine splitting. An INDO calcuration for a planar regular pentagonal ring configuration has shown the spectrum of the anion radical to give quintet lines with the relative intensity of 1 : 4 : 6 : 4 : 1 and hyperfine coupling constant of 28.085 gauss for the equivalent four protons and 0.084 gauss for equivalent four deuterons. The agreement between experimental and calculated results is satisfactory. Although the possibilities of the cation radical can not be ruled out completely at present, its INDO calculation[4] shows the spectrum to be quite different from the observed one. The comparison between b and c in Fig. 1 indicates the temperature-dependent motional narrowing.

Investigations for the α- and β-radical, as well as for the relation between trapped radicals and the intermediates of the radiolysis are being carried out.

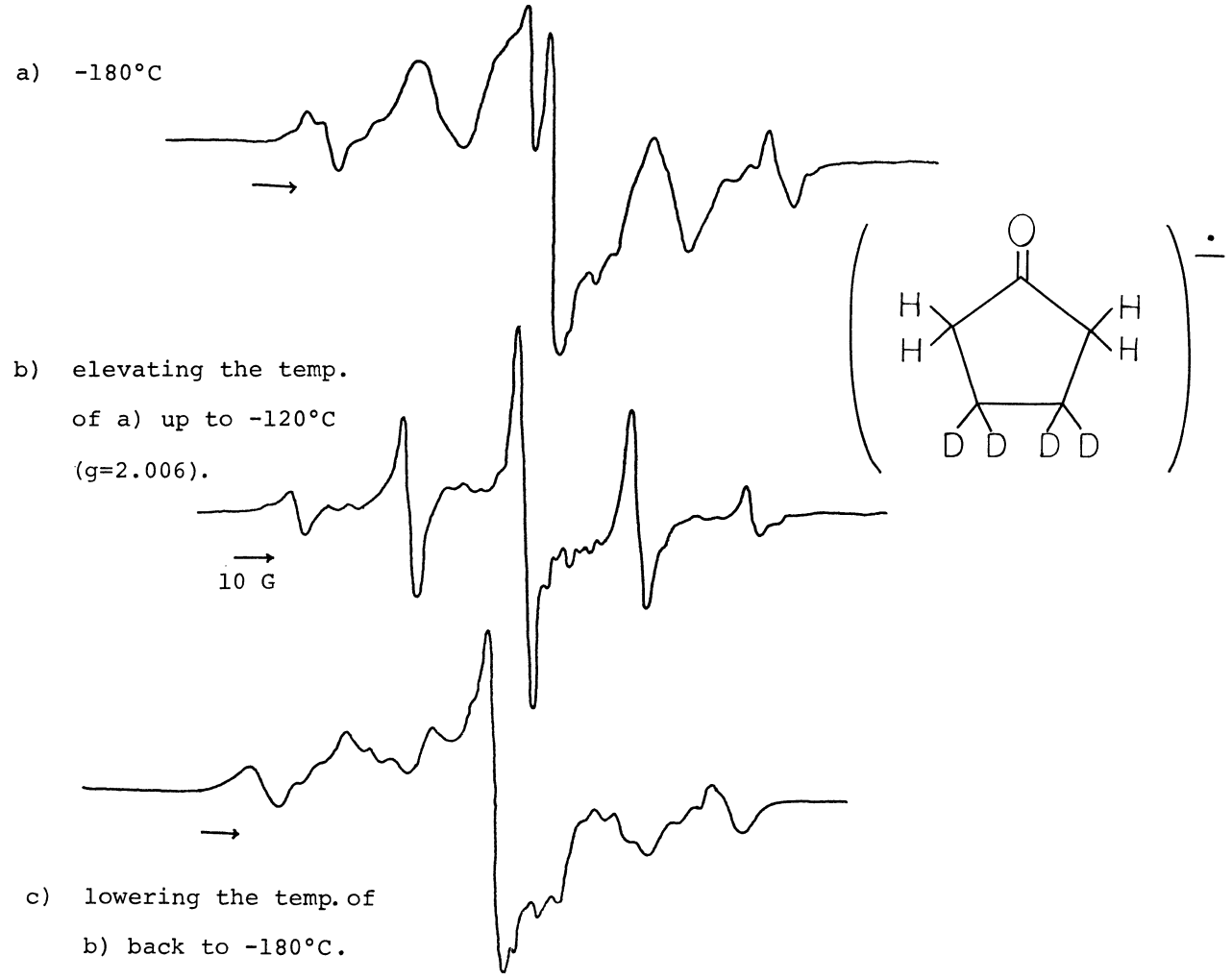


Fig. 1 ESR spectra of irradiated 3,3,4,4-cyclopentanone-$d_4$ observed at indicated temperatures.

## References

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1) For example, K. Unoura, M. Aikawa, and M. Katayama, Bull. Chem. Soc. Japan, 41, 1734(1968).

2) K. Unoura, M. Katayama, S. Shimada, H. Kashiwabara, and J. Sohma, The 8-th Symposium on ESR, Hiroshima, November, 1969.

3) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, J. Am. Chem. Soc., 80, 2326(1956).

4) J. A. Pople, and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970.

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