

TEMPERATURE DEPENDENCE OF ESR SIGNAL OF ISOPROPANOL RADICAL
FORMED BY UV IRRADIATION

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ESR signals of isopropanol radical were observed at various temperatures. Methyl groups of the radical were found to freely rotate down to 77 K, but to be in a frozen state at 4 K. Experimental results were discussed with the results calculated by INDO. A specially designed Dewar vessel was used for measurements at 77 K and 4 K.

The ESR signal of the isopropanol radical formed by UV irradiation of mixtures of acetone and isopropanol or of isopropanol and hydrogen peroxide was observed by Livingston and Zeldes¹⁾ at temperatures from 30°C to -42°C. Results showed that the six protons of two CH₃ groups of the radical are magnetically equivalent and give seven lines of the intensity ratio of 1:6:15:20:15:6:1 with a hyperfine coupling constant (HFCC) of ca. 20 G. These results suggest the free rotation of CH₃ groups. In the present study we observed ESR signals of isopropanol radical in a wider temperature range down to 4 K to examine the rotational state of CH₃ groups. Results are discussed in connection with HFCC calculated by INDO for various configurations of CH₃-proton.

Experimental. A mixture of acetone and isopropanol in 1:1 volume ratio was used. The ESR spectrometer was Varian E-4. For room temperature measurements the mixture was freed from oxygen by being bubbled with nitrogen, and then introduced into a flat ESR cell in the cavity by a flow technique. The measurement was conducted under the irradiation of UV. For lower temperature measurements the mixture in the ESR cell of 2.6 mm diameter tube, deaerated and sealed in vacuo, was gradually cooled to liquid N₂ temperature, under the UV irradiation for about 15 minutes. The mixture was then warmed up to -160°C in order to be freed from radicals except for the isopropanol radical, and served for ESR measurements at 77 K and 4 K.

Recently, Matsumura et al.²⁾ reported a Dewar vessel which can function at liquid He temperature in the cavity of X-band ESR. We have designed a simpler Dewar

device as shown in Fig. 1. The device consists of three Dewar vessels, A, B and C, to prevent the trouble caused by bubbling of liquid N_2 . Vessels A and C fixed inside the cavity by the aluminum jacket, were first cooled about -180°C by passing N_2 gas with a flow rate of $1\text{ m}^3/\text{hr}$ via a column immersed in liquid N_2 . Liquid He was introduced into vessel B which was immersed in another Dewar vessel of liquid N_2 . Vessel B filled with liquid He was then fixed into the cavity. Direct transfer of vessel B into A did not cause any trouble owing to the vaporization of liquid He. It takes about 6 hours for the full consumption of liquid He (300 ml) in vessel B by evaporation.

The present Dewar vessels were prepared by the evacuation to an order of 10^{-7} torr. at 200°C for a few days.

Experimental Results. The ESR signal at room temperature reproduced a signal of 7 lines with ca. 20 G separation to each other by Livingston and Zeldes.¹⁾ The signal obtained at 77 K is shown in Fig. 2, which shows 5 lines of 20 G separation with broad line width and intensity ratio which is close to the result at room temperature.¹⁾ Two other lines at the both ends were not clearly detected because of their small intensity as expected from the relative intensity ratio estimated by the binomial distribution. Figure 3 shows the results observed at 4 K, in which the separation of each lines and their relative intensity ratio are not equivalent to the results at higher temperatures. A broken line in Fig. 3 indicates the background of which large inclination was reduced by replacing the gold-plating attached on the wall of the cavity.

Calculated Results. Hyperfine coupling constants (HFCC) were calculated by INDO with standard bond lengths and bond angles³⁾ for different configurations of the radical. The isopropanol radical is concluded to have the lowest energy when OH stays in sp^2 plane of $>\dot{\text{C}}-$ with $\angle\text{COH} = 109^\circ 28'$. The calculated results for different configurations of CH_3 -proton (Cases I to V) are given in Table 1. The average HFCC values of CH_3 -proton and of OH-proton are found to be 23 G and -2 G respectively,

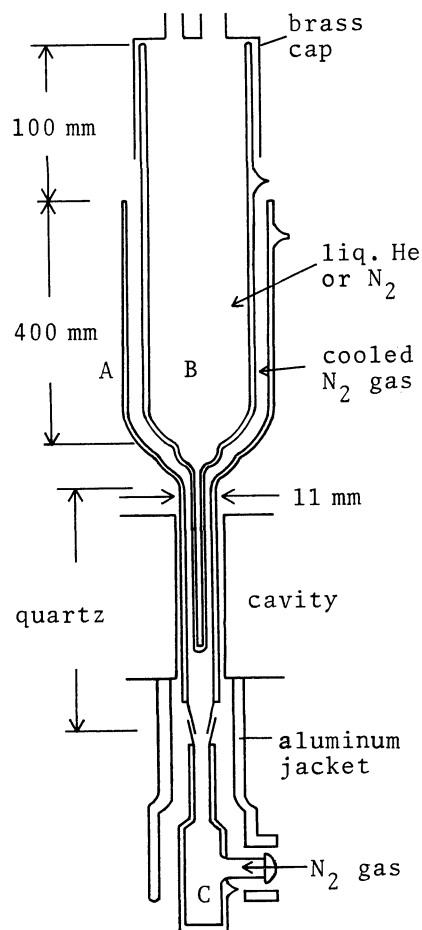


Fig. 1. A Dewar device for ESR measurements.

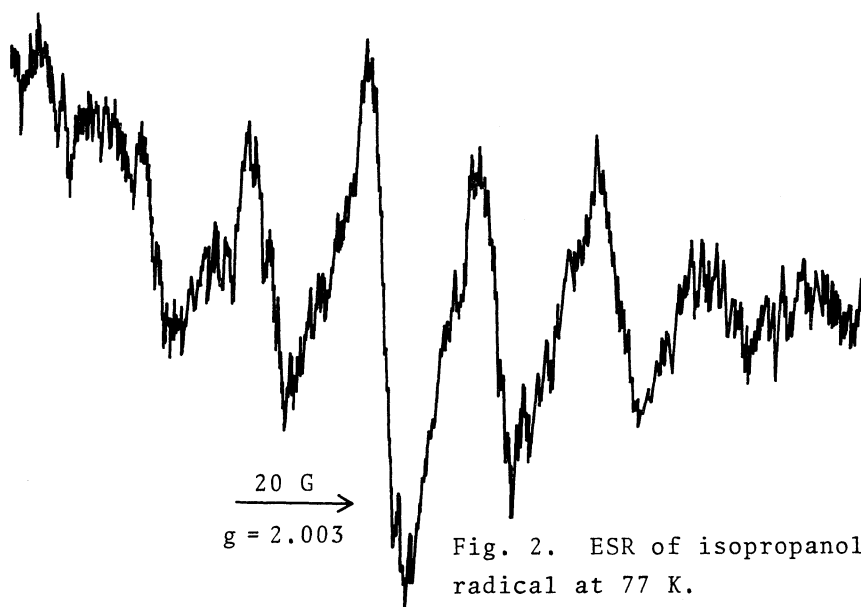


Fig. 2. ESR of isopropanol radical at 77 K.

both being irrespective of the rotational position of CH_3 -groups.

Discussion. The average HFCC value of CH_3 -proton in Table 1 agrees with the experimental value of ca. 20 G measured at $T > 77$ K. This tells that CH_3 groups of the radical freely rotate. The calculated HFCC of OH-proton (-2 G) agrees with experimental results.¹⁾ Experimental result at 4 K, however, differs from

that observed at 77 K which is simulated under the free rotation (Fig. 4, curve 1). Therefore, the rotation is frozen at 4 K. One of the three protons in CH_3 group has HFCC of ca. 42 G and the other two protons have that of 13-15 G (see Fig. 3). These values are satisfactorily reproduced by the configuration of Case III or IV in Table 1, where one of the three planes including $\dot{\text{C}}-\text{C}-\text{H}$ is normal to sp^2 plane of $>\dot{\text{C}}-$. Curve 2 in Fig. 4 represents the isotropic simulation that HFCC's of each two CH_3 -protons are 14.5, 15.5 and 42 G respectively. Comparison of Figs. 2 ~ 4 gives a good correspondence between the experimental and theoretical results, showing that the rotation of CH_3 group is frozen at 4 K and therefore the rotational barrier energy is between 77 K and 4 K in kT. The total

Table 1. Hyperfine Coupling Constant (HFCC) and Total Energy of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ Calculated by INDO

	CASE I ecli-ecli	CASE II stag-stag	CASE III	CASE IV	CASE V ecli-stag
HFCC of CH_3 -proton	1.5(1) G. 1.6(1) 33.2(4)	1.3(2) 34.0(4)	11.7(2) 12.5(2) 44.5(2)	11.8(2) 12.4(2) 44.4(2)	1.3(1) 1.4(1) 33.2(2) 34.0(2)
average HFCC of CH_3 -proton	23.3	23.5	22.9	22.9	23.3
HFCC of OH-proton	-2.1	-2.4	-2.0	-2.0	-2.0
total energy	-43.4148 A.U.		-43.4143	-43.4146	-43.4144

Ecli and stag stand for eclipse and staggered. Value in () represents the number of protons which give the same HFCC. Rotation of two CH_3 groups are; Case III, 30° , 30° from eclipse and Case IV, -30° , 30° from eclipse.

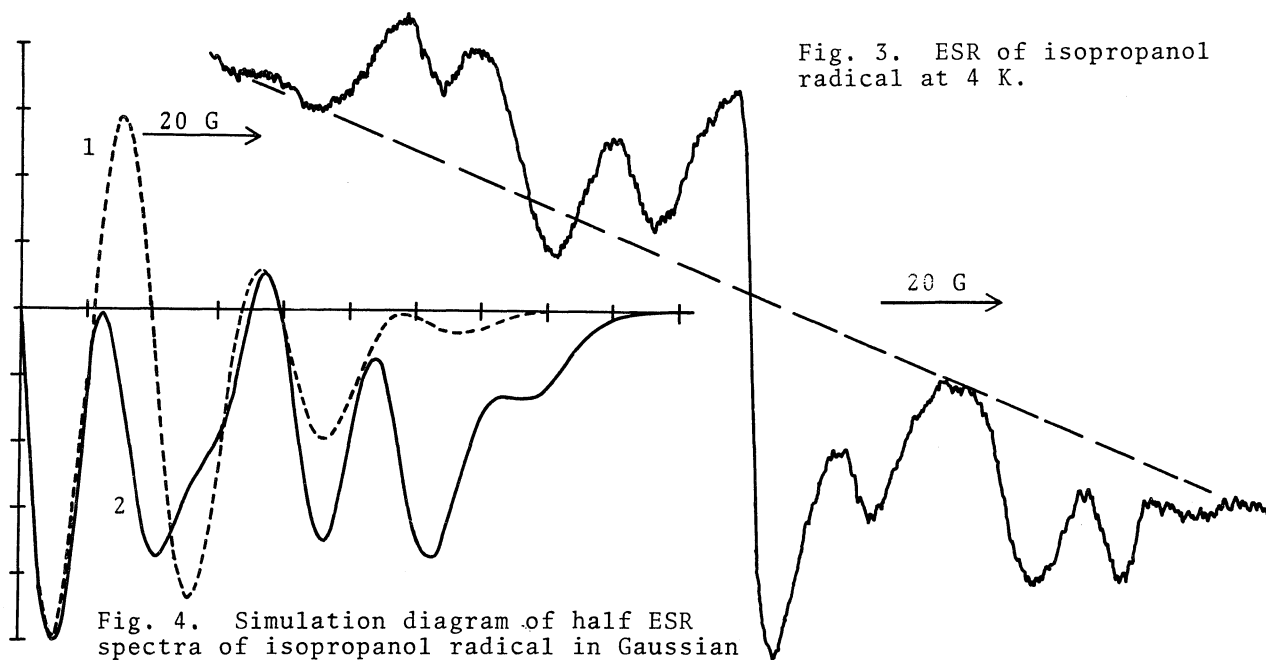


Fig. 3. ESR of isopropanol radical at 4 K.

Fig. 4. Simulation diagram of half ESR spectra of isopropanol radical in Gaussian type. Line width: 13.5 G, curve 1: free rotation of CH_3 -proton ($\text{HFCC} = 20 \text{ G}$), and curve 2: frozen rotation.

energy calculated by INDO is not the lowest for Case III or IV as seen in Table 1. This may be ascribed to the present values used for standard bond lengths and/or bond angles; i.e., they may not sufficiently reflect real values of the isopropanol radical.

In summary, it is concluded that the isopropanol radical is in a frozen state at 4 K and its configuration is given by Case III or IV in Table 1. On account of the very small rotational energy of CH_3 group, it will be expected that CH_3 groups of the adsorbed isopropanol radical⁴⁾ is in free rotational state although these groups have been concluded to face the electrode surface during the electrochemical reduction of acetone on mercury in acidic solutions.

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