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AN ESR STUDY ON PYRAMIDAL INVERSION AT THE TERVALENT CARBON ATOM OF 2-METHYL-1,3-DIOXOLAN-2-YL RADICAL

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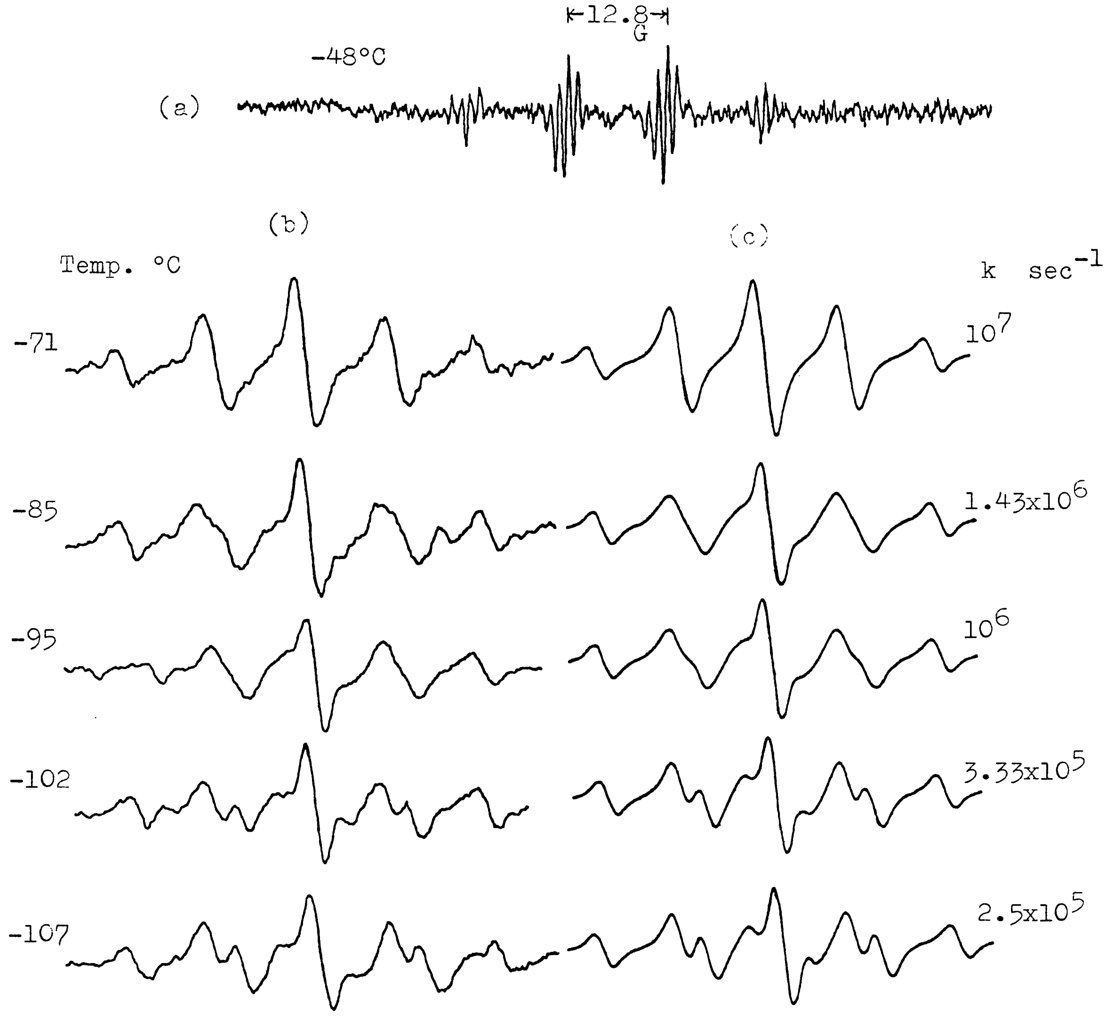
The effect of temperature on the esr spectrum of 2-methyl-1,3-dioxolan-2-yl radical was investigated. At low temperature, the four γ-hydrogens of this radical were observed to be two non-equivalent groups of two equivalent hydrogens. The radical centre undergoes a pyramidal inversion with an enthalpy of activation of 5.6 kcal/mole and an entropy of activation of 1.0 e.u.

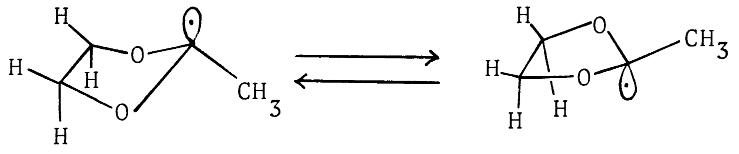
Chemical evidence has been presented for the pyramidal nature of the radical centre of the 2,4-dimethyl-1,3-dioxolan-2-yl radical.$^{1)}$ A pyramidal structure of the radical centre of 2-methyl-1,3-dioxolan-2-yl radical has been deduced on the basis of esr hyperfine splitting measurements;$^{2)}$ however, the non-equivalence of the four γ-hydrogens, which is expected from a pyramidal structure of the radical centre, has not been observed. We now report observation of the non-equivalence of the four γ-hydrogens in the 2-methyl-1,3-dioxolan-2-yl radical.

A mixture of 2-methyl-1,3-dioxolane (1 part), di-t-butyl peroxide (10 parts) and isopentane (10 parts) was degassed by a freeze-thaw technique on a vacuum line, and esr measurements were carried out during irradiation of the sample with a 400-watt high-pressure mercury lamp. Fig. 1(a) illustrates the esr spectrum of the 2-methyl-1,3-dioxolan-2-yl radical at -48°C, which consists of a quartet with $a(\beta\text{-H}) = 12.8$ G due to hyperfine coupling with the 2-methyl group, and each of the quartet is further split into a quintet with $a(\gamma\text{-H}) = 1.1$ G owing to coupling with the four equivalent γ-hydrogens. When the temperature was decreased, each peak of the quintet broadened gradually until at -95°C a coalescence temperature was reached, as shown in Fig. 1(b). Below the coalescence temperature, a nine-line spectrum began to be observed which approached to a 1:2:2:1:4:1:2:2:1 triplet (1.24 G) of triplets (0.91 G). These findings are readily explained in terms of a

Figure 1. (a) First derivative esr spectra of the 2-methyl-1,3-dioxolan-2-yl radical. (b) The second or third quintet in (a) is expanded ten times. (c) Calculated esr spectra.



rapid inversion of the pyramidal radical centre of the 2-methyl-1,3-dioxolan-2-yl radical which is shown in the envelope form:



Evidently, the inversion, which is very rapid at higher temperatures and makes the four γ-protons appear equivalent, becomes slower with a decrease in temperature and finally at -107°C slow enough for the four protons to be observed as behaving as two different sets of two equivalent protons. The rates of inversion were estimated by computer simulation of the shapes of the spectra at different temperatures using the method developed by Carrington on the basis of the Bloch equations.³⁾ From the temperature dependence of the rate (k $\sec^{-1}$) shown in Fig. 2, the activation parameters were obtained:

$$\Delta H^{\ddagger} = 5.6 \pm 0.2 \text{ kcal/mole} \quad \text{and} \quad \Delta S^{\ddagger} = 1.0 \pm 1.0 \text{ e.u.}$$

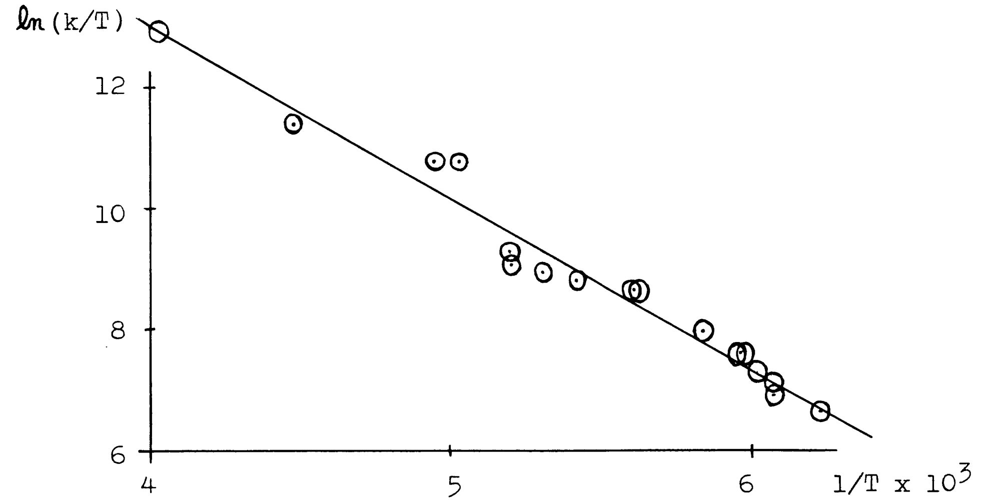


Figure 2. Least-squares plot of ln(k/T) vs. 1/T for the interconversion shown in Figure 1.

An alternative possibility, which is shown schematically in Fig. 3, might be that, although the radical centre inverts its pyramidal structure very rapidly or rather is planar, the interconversion between the half-chair conformations is so slow that the two pseudo-axial hydrogens are distinguishable from the two pseudo-equatorial hydrogens by esr spectroscopy. This possibility, however, is excluded by the relatively high value of $\Delta H^{\ddagger}$ = 5.6 kcal/mole, because the interconversion is brought about by pseudorotation of the five-membered ring structure, and the

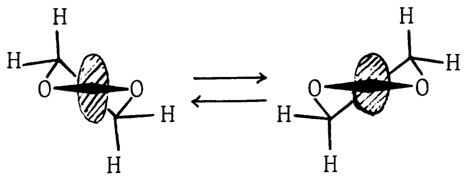


Figure 3. Shaded areas represent the 2-methyl group which is flipping very fast or the planar radical centre.

pseudorotation is generally known to have an extremely low energy barrier; indeed, the barrier for 1,3-dioxolane is estimated at only 120 cal/mole, which is tantamount to free pseudorotation.$^{4)}$

An envelope form being assumed for the 2-methyl-1,3-dioxolan-2-yl radical, the INDO MO calculation$^{5)}$ with two structural parameters, θ and ψ, as defined in Fig. 4, gave hyperfine coupling constants: $a(\beta\text{-H})=+12.8$ G (the mean of the constants for H_7, H_8, and H_9), $a(H_{10}$ or $H_{12}) = -0.86$ G, and $a(H_{11}$ or $H_{13}) = +1.18$ G in excellent agreement with the observed values, when $\theta = 46°$ and $\psi = 107.5°$.

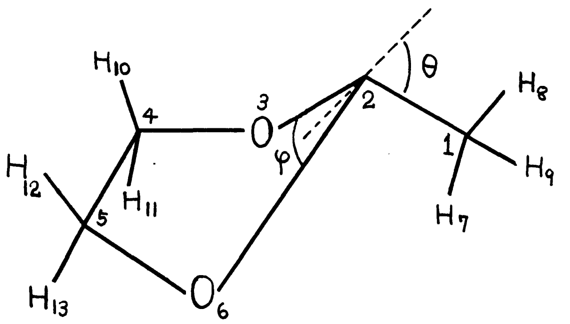


Figure 4. Structural parameters for an envelope form of the 2-methyl-1,3-dioxolan-2-yl radical. The following distances and bond angles were used:$^{6)}$ (a) $C_1C_2=1.53$ Å, $C_2O_3=1.395$ Å, $O_3C_4=1.415$ Å, $C_4C_5=1.534$ Å, and CH=1.09 Å; (b) all of the HCH angles and the C_2C_1H angle are tetrahedral; (c) the $H_{10}C_4H_{11}$ and $H_{12}C_5H_{13}$ planes bisect the $O_3C_4C_5$ and $O_6C_5C_4$ angles, respectively; (d) the two COC angles are 110°.

References

(1) S. O. Kobayashi and O. Simamura, Chem. Lett., 695 (1973).
(2) A. J. Dobbs, B. C. Gilbert and R. O. C. Norman, J. Chem. Soc. (A), 124 (1971).
(3) A. Carrington, Mol. Phys., 5, 425 (1962).
(4) J. R. Durig and D. W. Wertz, J. Chem. Phys., 49, 675, 2118 (1968);
J. A. Greenhouse and H. L. Strauss, J. Chem. Phys., 50, 124 (1969).
(5) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill Book Co., New York, N. Y., 1970, p. 128.
(6) Cf. S. Furberg and O. Hassel, Acta Chem. Scand., 4, 1548 (1950).

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