CHEMISTRY LETTERS, pp. 805-808, 1974. Published by the Chemical Society of Japan

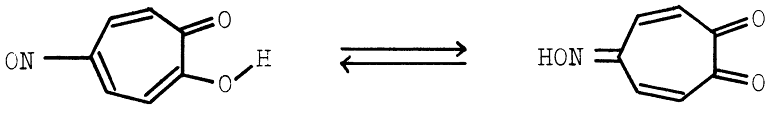
RESTRICTED ROTATION IN 5-NITROSOTROPOLONE AND THE ANION RADICAL

Yusaku IKEGAMI and Toyonobu ASAO*
Chemical Research Institute of Non-Aqueous Solutions,
Tohoku University, Katahira-2-chome, Sendai 980
* College of General Education, Tohoku University,
Kawauchi, Sendai 980

The ESR study of the 5-nitrosotropolonate anion radical generated electrolytically in N,N-dimethylformamide elucidated the restricted rotation around the C-N bond. The free energy of activation $\Delta G^{\ddagger}$ for the rotation of 5-nitrosotropolone was estimated by the NMR study to be 16.5 kcal.mol^{-1} in dimethylsulfoxide.

5-Nitrosotropolone (I) shows a peculiar infrared spectrum with strong and broad absorption bands at 1602, 1318, and 1026 cm^{-1}, though the OH stretching absorption (3150 cm^{-1}) is in ordinary position for tropolone derivatives.$^{1)}$ It has also been known that I shows often the reactions as the tautomeric structure, tropoquinone monoxime (II).$^{2)}$ These facts would be explained by the strong intermolecular interaction in the solid state or by considering the reality of the tautomeric form.

In connection with the structure of I, this paper reports on the restricted rotation in the 5-nitrosotropolonate anion radical studied by electron spin resonance (ESR) technique, together with that in I shown by the NMR study.



I II

Electrolysis of 5-nitrosotropolone in N,N-dimethylformamide (DMF), using tetra-n-propylammonium perchlorate as the supporting electrolyte, produced the anion radical which exhibited a strong ESR signal. The ESR spectrum shown in Fig. 1 is interpreted as that of the tropolonate anion radical in a similar manner to the case of the nitrotropolonate anion radicals.$^{3)}$ Hyperfine structure of the spectrum is analyzed with four splitting constants, one of which represents the coupling with one nitrogen atom and others the couplings with a pair of equivalent hydrogen atoms and with two nonequivalent hydrogen atoms.

The nonequivalence of latter two hydrogen atoms may be explained if the nitroso group is assumed to be planar with the seven-membered ring and there is some interaction between the nitroso group and one of the adjacent protons, as depicted in III. To rationalize the weak interaction and to assist the assignment for the splitting constants, the spin density calculations were carried out. The interaction between the nitroso group and an adjacent proton can be included in a Hückel MO calculation of the spin densities in a way which describes the polarization effects of the nitroso group by changing Coulomb integral at the 4-carbon atom (α-effect).[4,5] A reliable result was obtained by adopting the α-effect to the MO calculation followed by the McLachlan procedure[6] as follows.

The resonance (β_{ij}) and Coulomb integral parameters (α_i) appropriate to the C⩵O groups of the tropolonate ion have been found out for the nitrotropolonate anion radicals.[3] The values for the C-N=O group can be chosen from those recommended by Rieger and Fraenkel,[7] but with $\alpha_N = \alpha + 1.2\beta$ [8] which was satisfactory to the present calculation. Then, some sets of the McLachlan calculations with various Coulomb integrals ($\alpha_4 = \alpha - h_4\beta$) for 4-position were performed to obtain reasonable agreement with the experimental spin densities. The appropriate parameter for 4-position was thus found out to be around $h_4 = 0.18$. The spin densities calculated with this value are given in Table 1.

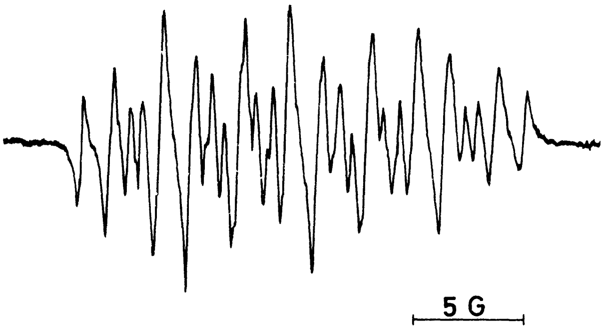


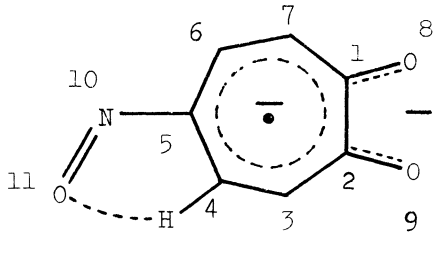
Fig. 1. ESR spectrum of the 5-nitrosotropolonate anion radical generated by the electrolysis in DMF.

Table 1. Observed Splitting Constants ($\underline{a}_i$) and Calculated Spin Densities (ρ_i) for the 5-Nitrosotropolonate Anion Radical

Position	$\underline{a}_i$	Spin density, ρ_i	
	gauss	Exptl.[a)]	Calcd.[b)]
1			0.1120
2			0.0871
3	1.36	0.0574	-0.0484
4	2.30	0.0970	0.0975
5			-0.0482
6	3.70	0.1561	0.1549
7	1.36	0.0574	-0.0606
8			0.0478
9			0.0374
10			0.2789
11			0.3417

a) With the relation $\underline{a}_i = \underline{Q}^H_{CH}\rho_i$, in which $|Q^H_{CH}| = 23.7$ gauss was adopted.

b) Parameters for the calculation: $\alpha_8 = \alpha_9 = \alpha + 2.0\beta$, $\beta_{1,8} = \beta_{2,9} = 1.8\beta$, $\beta_{5,10} = 1.2\beta$, $\alpha_{11} = \alpha + 1.24\beta$, $\beta_{10,11} = 1.67\beta$, $\alpha_{10} = \alpha + 1.2\beta$, $\alpha_4 = \alpha - 0.18\beta$, and $\lambda = 1.2$.



III

It is noteworthy that the calculation required the larger parameter h_4 than that for the nitrosobenzene anion radical.[8,9] This may be interpreted by that the distance between the nitroso oxygen and the nearby carbon of tropolonate ring is smaller than that of benzene ring.

Thus, the ESR study on the anion radical demanded the assumption of the restricted rotation around the C-N bond in terms of the spectrometer frequency. This assumption is also required to interprete the NMR spectrum of 5-nitrosotropolone in dimethylsulfoxide (DMSO) or in a mixed solvent of DMSO and acetone. So, the temperature dependence of the NMR spectrum was examined. The spectra in DMSO-d_6 are shown in Fig. 2. In the spectrum at 35°C, H_4 and H_6 proton signals dissmilarly appear at δ 7.76 and 7.27 ppm (chemical shift difference $\nu_4 - \nu_6 =$ 45 Hz) as doublet with the same coupling constants J = 11.9 Hz, respectively, and H_3 and H_7 proton signals appear at δ 6.6 ppm as doublet with J = 11.9 Hz.

A rise in temperature results in coalescence of the H_4 and H_6 proton signals and further heating finally generates a lone doublet locating halfway between ν_4 and ν_6. This phenomenon is characteristic of rapid exchange between two equally populated sites presumably arised from the restricted rotation around the nitroso C-N bond.

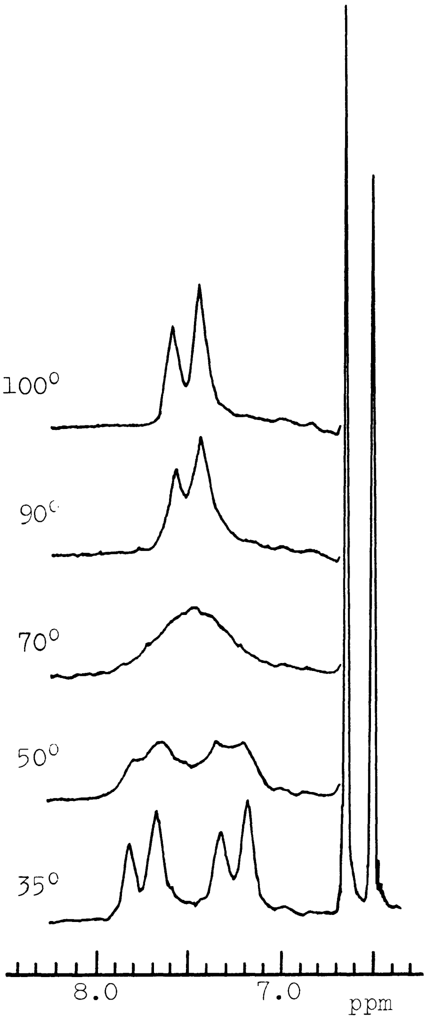


Fig. 2. NMR spectra of 5-nitrosotropolone in DMSO-d_6 at various temperatures.

From the relation $k^1 = \pi\Delta\nu/\sqrt{2}$, the rate constant k^1 at coalescence temperature T_c will be calculated. The free energy of activation $\Delta G^{\ddagger}$ can be derived from the transformed equation of the Eyring equation:[10]

$$\Delta G^{\ddagger} = 2.303RT_c(10.319 - \log_{10}k^1 + \log_{10}T_c).$$

The calculated values of k^1 and $\Delta G^{\ddagger}$ are 100.0 sec^{-1} and 16.5 kcal•mol^{-1}, respectively, with T_c = 333°K for 5-nitrosotropolone in DMSO-d_6.

When the NMR spectrum was measured in a mixed solvent of DMSO-d_6 and acetone-d_6 (2 : 1) $\Delta\nu$ and T_c were obtained as 49 Hz and 373°K, therefore, k^1 and $\Delta G^{\ddagger}$ are calculated as 108.9 sec^{-1} and 18.5 kcal•mol^{-1}.

These $\Delta G^{\ddagger}$ values are comparable but a little higher than those obtained for p-substituted nitrosobenzenes ($\Delta G^{\ddagger}$, 10-13 kcal•mol^{-1}).[11,12] The increase in the rotational barrier with decrease in solvent dielectric constant implies that the rotation proceeds through a transition state having more dipolar character which may be stabilized by polar solvent than the ground state.

The authors thank Professor Shuichi Seto for his helpful discussion.

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(Received May 14, 1974)