ESR Spectrum of Tropone Anion Radical

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Tropone is a particularly interesting compound in which to compare experimentally and theoretically estimated pi-electron densities because it is a peculiar conjugate ring system. The Hückel MO treatment for tropone molecule results in that the unpaired electron in its anion radical does not distribute to the carbonyl group.$^{1)}$ This fact is likely related to the instability of the anion radical. Treatment of tropone, for example, with alkali metal in degassed tetrahydrofuran or dimethoxyethane displays the immediate color change into reddish-violet solution, but it does not show any ESR signal. This paper reports the ESR spectrum of tropone anion radical prepared with the electrolytic technique, which have proven a valuable tool for the preparation of radical ions for ESR study.$^{2)}$

Tropone was thoroughly purified by distillation in a high-vaccum apparatus. The electrochemical reduction of the solution in degassed *N,N*-dimethylformamide (DMF) presented the spectrum shown in Fig. 1. Tetra-*n*-propylammonium perchlorate was used as the supporting electrolyte. The radical is not so stable that the signal strength decreased to one half during 15 min at room temperature after the current was shut off.

Hyperfine structure of the spectrum is analyzed with three splitting constants, which are reasonably assigned in consideration of the calculated spin densities, as given in Table 1. The calculations of unpaired spin densities (ρ_i^π) for tropone anion radical were carried out by Hückel and McLachlan's methods$^{3)}$ on some cases changed Coulomb integral parameter (α_O) at oxygen atom and resonance integral parameter ($\beta_{C=O}$) of C=O bond. We neglected all other bond length variations. The parameters given for the carbonyl group do not affect so much on the spin densities of carbon atoms at 2-, 4-, 5- and 7-positions. A good results is shown in Table 1 in which the parameters, $\alpha_O = \alpha + 1.8\,\beta$ and $\beta_{C=O} = 1.4\,\beta$, were applied for the calculation.

TABLE 1. OBSERVED SPLITTING CONSTANTS AND CALCULATED SPIN DENSITIES FOR TROPONE ANION RADICAL

Ring position (Number of H)	Observed a_i^H gauss	Spin density, ρ_i^π		
		Experimental$^{a)}$	Calculated	
			Hückel	McLachlan
1			0	−0.05342
2, 7 (2H)	8.578	0.3619	0.27157	0.37221
3, 6 (2H)	0.10	0.004	0.05379	−0.02019
4, 5 (2H)	5.050	0.2131	0.17464	0.18427
8			0	−0.01916

a) Spin densities using the relation, $a_i^H = Q_{CH}^H \rho_i^\pi$, where $|Q_{CH}^H| = 23.7$ gauss.

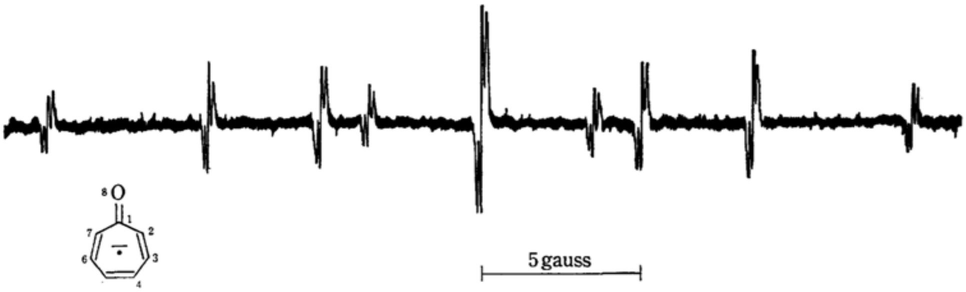

Fig. 1. ESR spectrum of tropone anion radical generated by the electrolytic reduction in DMF.

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1) H. Yamaguchi, Y. Amako and H. Azumi, *Tetrahedron*, **24**, 267 (1968).

2) For example, M. Hirayama, This Bulletin, **40**, 1822 (1967).

3) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960). The λ-parameter in McLachlan's procedure was fixed at the value $\lambda = 1.2\,\beta$.