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THE ESR SPECTRA OF THE ANION RADICALS OF 2-METHOXYTROPONE AND ITS DERIVATIVES

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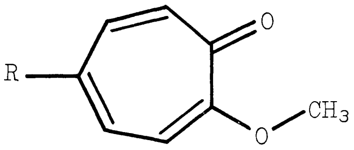
The ESR spectrum of the 2-methoxytropone anion radical has been examined. The radical was generated by electrolytic reduction of the neutral species in N,N-dimethylformamide. Hyperfine splitting constants of the ESR spectrum were reasonably assigned by comparison with the calculated spin densities. 5-Methyl, 5-isopropyl, and 5-nitro derivatives of 2-methoxytropone have also been examined in a similar way.

In the previous paper,[1)] an electron spin resonance (ESR) study of the tropone anion radical was reported. The success of generation of the radical led us to the similar examination for tropone derivatives. This paper reports the ESR study on the anion radicals of 2-methoxytropone (I) and its derivatives, II, III, and IV, which were prepared in relatively stable forms as far as we have tried for many tropone derivatives.



I: R = H
II: R = CH_3
III: R = $CH(CH_3)_2$
IV: R = NO_2

2-Methoxytropone Anion Radical. Treatment of I with an alkali metal in degassed 1,2-dimethoxyethane or tetrahydrofuran caused immediate change in color to a reddish violet at temperatures above -40°C. However, no ESR signal was observed in this treatment. In a similar manner as the generation of the tropone anion radical,[1)] the electrolytic reduction of I in degassed N,N-dimethylformamide (DMF) at room temperature gave the ESR spectrum shown in Fig. 1. The radical is not stable so that the signal intensity decreased to one half during 30 min at room temperature after the current was turned off. The color of the solution changed gradually to a purple during the electrolysis. Lowering the temperature to -50°C was not favorable for getting a better resolution of the spectrum.

The ESR spectrum affords only two splitting constants one of which (8.3 gauss) represents the coupling with one hydrogen atom and another (4.9 gauss) the coupling with two equivalent hydrogen atoms. Assignments for the constants are given on the basis of the spin density calculations.

Calculation of unpaired spin densities for the 2-methoxytropone anion radical was carried out by the Hückel MO theory, followed by the McLachlan procedure,[2)] using some Coulomb and resonance integral parameters for the carbonyl and methoxy groups. All other bond length variations were neglected. Considering the experimental result that the spin densities at two ring carbon atoms would be close each other, the good figures were obtained when the parameters proposed by Streitwieser[3)] were used for the calculation by the McLachlan procedure. The splitting constants and the spin densities are given in Table 1.

Table 1. Observed Splitting Constants (a_i) and Calculated Spin Densities (ρ_i) for the 2-Methoxytropone Anion Radical

Position	a_i gauss	Spin density, ρ_i Exptl.[a)]	Calcd.[b)]
1			-0.0550
2			0.3699
3			-0.0402
4	4.9	0.207	0.2088
5	4.9	0.207	0.1714
6			-0.0192
7	8.3	0.350	0.3676
8			-0.0255
9			0.0222

a) With the McConnell relation, $a_i = Q_{CH}^{H} \rho_i$, in which $Q_{CH}^{H} = 23.7$ gauss was adopted.

b) McLachlan spin density. Parameters for the calculation: $\alpha_8 = \alpha + \beta$, $\beta_{1,8} = 1\beta$, $\alpha_9 = \alpha + 2\beta$, $\beta_{2,9} = 0.8\beta$, and $\lambda = 1.2$.

Fig. 1. ESR spectrum of 2-methoxytropone anion radical generated by the electrolytic reduction in DMF.

Anion Radicals of 5-Methyl- and 5-Isopropyl-2-methoxytropones. Both 5-methyl- (II) and 5-isopropyl-2-methoxytropones (III) generated the corresponding anion radicals by the electrolytic reductions in the same way as the anion radical of I. The ESR spectra are shown in Fig. 2. For the compound II, when a direct current of ca. 2.8V was applied for a long period, a gradual production of another paramagnetic species was observed in the ESR spectrum. The unknown species is more stable than the anion radical of II.

The observed splitting constants are given in Table 2, in which the assignments were given by a comparison of the constants with those for the 2-methoxytropone anion radical. It is remarkable that the methyl proton splitting constant is quite large as compared with that of methine proton of the isopropyl compound.

5-Nitro-2-methoxytropone Anion Radical. It is generally known that nitro aromatic compounds are reduced easily to produce the stable anion radicals. So the generation of a stable anion radical is expected for the compound IV.

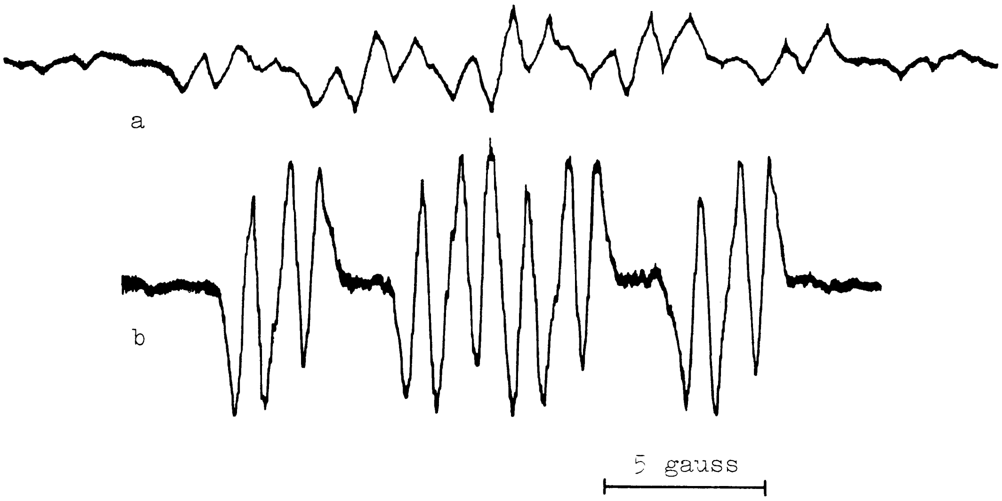


Fig. 2. ESR spectra of the anion radicals of 5-methyl-2-methoxytropone (a) and 5-isopropyl-2-methoxytropone (b) in DMF.

Table 2. Observed Splitting Constants ($\underline{a}_i$) for the anion radicals of 5-Methyl- (II), 5-Isopropyl- (III), and 5-Nitro-2-methoxytropones (IV)

Position	$\underline{a}_i$ gauss II	III	IV
3	1.1	1.12	1.10
4	5.2	5.40	6.42
6	----	----	0.12
7	8.3	8.70	1.46
9 ($OC\underline{H}_3$)	----	----	0.75
$C\underline{H}_3$	4.1	----	----
$C\underline{H}(CH_3)_2$	----	0.87	----
$\underline{N}O_2$	----	----	3.36

Treatment of IV with lithium or sodium metal in degassed 1,2-dimethoxyethane showed neither change in its color nor the appearance of ESR signal. On the other hand, the electrolytic reduction of IV in DMF showed a strong ESR signal, while the yellow color of the solution turned dark brown gradually during the electrolysis. The ESR spectrum is shown in Fig. 3. The radical is comparatively stable as compared with the anion radicals of I, II, and III. However, the electrolysis for a long period at ca. 2.8V led to the generation of another paramagnetic species. The ESR hyperfine structure of the second paramagnetic species consists of 21 hyperfine lines and is the same with that of the radical generated by the electrolysis of 5-nitrotropolone in DMF,$^{4)}$ implying the generation of the 5-nitrotropolonate anion radical.

Hyperfine structure of the spectrum shown in Fig. 3 is analyzed with six splitting constants listed in Table 2. The analysis was confirmed by the spectral simulation with a half width of 100 milligauss. The nitrogen splitting constant (3.36

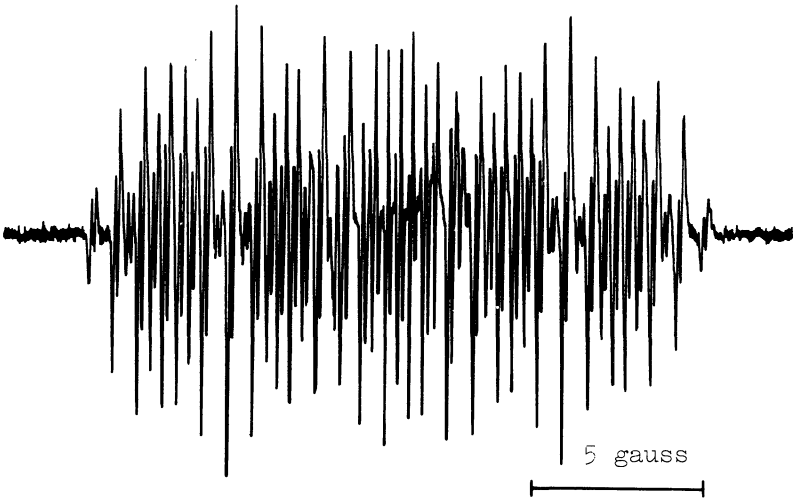


Fig. 3. ESR spectrum of 5-nitro-2-methoxytropone anion radical in DMF.

gauss) was readily assigned according to the type of splitting. Other assignments were given tentatively on the basis of the calculated spin densities by the Hückel MO theory. The Hückel MO calculation followed by the McLachlan procedure was carried out in order to estimate the spin density distribution. However, the use of the values of parameters for the nitro group adopted by Rieger and Fraenkel[5] and the values for 2-methoxytropone above-mentioned did not show the excellent agreement between the observed and calculated spin densities, though the assignments were given readily as indicated in Table 2.

Conclusion. Few studies on the anion radicals of tropone and its derivatives have been reported.[1,6,7] The radicals are generally unstable and could only be generated by electrochemical reduction in DMF under the existence of a large amount of supporting electrolyte,[1,6] except the case that tropone was reduced to the anion radical by dimethylsulfoxide solution of potassium t-butoxide.[7] The splitting constants for each radical of tropone, 2-methoxytropone, 5-methyl-2-methoxytropone, and 2,7-dimethyltropone[6] are large firstly at 2- and 7-positions (8.3-8.8 gauss) and secondarily at 4- and 5-positions (4.7-5.4 gauss). It is thus clear that the spin distribution in such radicals could be understood qualitatively on the basis of the calculations for the tropone anion radical. However, it must be noticed that the spin distribution in tropone ring is seriously affected by the introduction of a nitro group.

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