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II*. SPECTRAL STUDIES AND EXTENDED HÜCKEL CALCULATIONS ON SUBSTITUTED BENZOYLCYCLOPENTADIENYLMANGANESE TRICARBONYL ANIONS**

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Summary

ESR studies and extended Huckel molecular orbital calculations have been carried out on the radical anion of benzoylcyclopentadienylmanganese tricarbonyl and on the mono- and di-methyl substituted derivatives. A good agreement between the calculated and observed hyperfine constants is observed. The results support the view that there is extensive electron delocalization over the molecule with most of the spin density on the manganese atom the ketonic group and the phenyl ring. The change in spin density distribution on varying the substituent position shows that the major effect is electronic in nature.

Introduction

In the first paper [1] of this series ESR studies of anion radicals of benzoylcyclopentadienylmanganese tricarbonyl and some methyl substituted (on the cyclopentadienyl ring) derivatives were reported. In this paper a more detailed study of these radicals along with the anion radicals with methyl substituents at various positions on the phenyl ring is reported. This was undertaken to elucidate the effect of substituents on spin delocalization. In addition semi-empirical molecular orbital calculations have been carried out to study the unpaired electron delocalization over the entire molecular skeleton and to support the interpretation of ESR spectra. Computer simulation of the spectra was undertaken to obtain more accurate hyperfine coupling constants as the spectra were not fully resolved. The general background to this work can be found in reference 1.

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[*] For part I see ref. 1.

[**] Taken in part from the Ph.D. thesis of Chit Kay Chu, Memorial University of Newfoundland, 1974.

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Experimental

The parent compounds and the anion radicals were prepared by similar methods to that previously reported [1]. All the spectra were recorded on a JEOLCO ME 3X ESR spectrometer. The magnetic field was measured with an NMR gaussmeter. The frequency was measured by the beat method using a Micro—Now system. Both the microwave frequency and NMR frequency were measured with a TSI 385-R frequency counter. The following were typical instrument conditions used in recording the spectra; microwave power, 250 μW; modulation, 125 mG; sweep, 2 G per min; response time, 0.3 sec. In order to obtain optimum resolution the spectra were recorded at various temperatures using a JEOLCO JES-VT3 temperature control unit. However, in all the cases studied the room temperature spectra showed the best resolution. All the numerical calculations were carried out on an IBM 370/155 computer. QCPE programme number 210 (Quantum Chemistry Programme Exchange, Chemistry Department, Indiana University, Bloomington, Ind. 47401, U.S.A.) was used for simulating the spectra. All other programmes were written especially for this paper. For simulating the spectra, the output from the IBM 370/155 was recorded on a magnetic tape. This tape was then processed with a PDP-12 computer with a CALCOMP plotter attached to it.

All the spectra are interpreted using the spin Hamiltonian

$$\mathcal{H} = g\beta \mathrm{H} \times S + \sum_i A_i \times I \times S \tag{1}$$

where A_i is the hyperfine constant for the ith nucleus with nuclear spin I_i. The resonant magnetic fields can be obtained either by diagonalising the Hamiltonian or by the perturbation method. In the present case it is found that second order perturbation calculations yield satisfactory results. The spectra were simulated using both Lorentzian and Gaussian line shapes. In all the cases, the Lorentzian line shapes yield better agreement with experimental spectra.

MO calculations

The Extended Hückel Molecular Orbital (EHMO) method [2] is used to calculate the unpaired spin density. The various criticisms on this method are well documented [3, 4]. Due to the large size of the molecules, lack of overall symmetry, and the occurrence of *d*-orbitals, more sophisticated methods can not be used [5-7]. At the same time more primitive methods, like HMO, break down completely in the present case because of nonplanarity of the molecule and the heteroatomic composition of the molecule. Therefore the EHMO method was chosen as a compromise between the various methods.

The MO's are expanded as a linear combination of atomic orbitals.

$$\psi_i = \sum_j C_{ij}\phi_j \tag{2}$$

The eigen vectors C_{ij} are related to the spin densities. In order to calculate these quantities the basic sets of 1*s* orbitals for H, 2*s* and 2*p* orbitals for C and O [8] and 3*d*, 4*s* and 4*p* orbitals for Mn [9] are employed. The valence orbital ionization potentials [10] are chosen for the diagonal matrix elements. The off diagonal elements are calculated using Cusachs [11] approximation viz.

$$H_{ij} = (2-|S_{ij}|)\,(H_{ii} + H_{jj})\,S_{ij}/2 \qquad (3)$$

where the S_{ij}'s are the overlaps between the orbitals i and j.

The overlaps of neighbouring and next nearest neighbouring atoms were considered in the organic ligand. Only the neighbouring atom overlaps were considered in the rest of the molecule. Carbon monoxide orbitals [12] were used for the carbon monoxide groups attached to manganese.

The self-consistent charge (SCC) method was employed using the initial values given by Brown and Rawlinson [13] (i.e., 0.21 for Mn, 0.14 for Cr and $q(\mathrm{CO}) = -0.18$). Computer iteration to convergence was carried out for benzoylcyclopentadienylmanganese tricarbonyl. However, due to the size of the matrices, calculations for the other molecules were carried out to self-consistency by successive approximations.

Convergence was assumed if the difference between the computed and assumed charges was less than 0.005 units.

Results and discussion

The ESR spectra of the radicals with methyl substituents on the cyclopentadienyl ring at positions α and β have already been discussed [1]. These spectra show a six-line hyperfine structure due to ^{55}Mn (I = 5/2) (Table 1). Each of these hyperfine lines is further split into a doublet of triplets. The MO calculations (Tables 2 and 3) show that the density at the *para* proton is greater than that at the *ortho* proton while the densities at the site of other protons are very small. Therefore it is clear that the doublet must be due to the *para* proton while the triplet must be due to the two equivalent *ortho* protons. Further proof to

TABLE 1

EXPERIMENTAL VALUES OF g AND THE HYPERFINE COUPLING CONSTANTS (10^{-4} cm^{-1}) FOR THE ANION RADICALS $C_6H_4RCOC_5H_3UR'Mn(CO)_3^-$

R	R'	g	A(Mn)	A(*p* H)[a]	A(*o* H)[b]	A(H(CH$_3$))[c]
H	H	2.0001	7.71	2.94	1.06	—
H	α-CH$_3$	2.0001	6.19	3.49	0.87	—
H	β-CH$_3$	2.0001	7.79	3.02	1.06	—
o-CH$_3$	H	1.9990	11.86	<0.3	<0.2	—
p-CH$_3$	H	1.9992	9.04	—	<0.2	<0.3
o-CH$_3$	α-CH$_3$	1.9985	12.02	<0.5	<0.4	—
p-CH$_3$	α-CH$_3$	1.9995	7.76	—	<0.90	2.6
p-CH$_3$	β-CH$_3$	1.9996	9.08	—	<0.4	2.42
m-CH$_3$	H	1.9997	8.10	<0.05	<0.5	—
Benzene-*d*$_6$						
D	H	2.0001	7.74	<0.3	<0.2	—
D	β-CH$_3$	1.9989	7.26	<0.2	<0.2	—

[a] *Para* proton coupling constant. [b] *Ortho* proton coupling constant. [c] Proton coupling constant for CH$_3$

TABLE 2

CALCULATED UNPAIRED SPIN DENSITIES FOR $C_6H_4RCOC_5H_3R'Mn(CO)_3^-$ [a]

R	R'	Phenyl ring	Cyclopentadienyl ring	Mn
H	H	$\rho_1 = \rho_5 = 0.052$ $\rho_2 = \rho_4 = 0.011$ $\rho_3 = 0.120$ $\rho_6 = 0.091$	$\rho_7 = 0.026$ $\rho_8 = \rho_{11} = 0.006$ $\rho_9 = \rho_{10} = -0.003$	0.200
H	α-CH_3	$\rho_1 = \rho_5 = 0.042$ $\rho_2 = \rho_4 = 0.009$ $\rho_3 = 0.134$ $\rho_6 = 0.080$	$\rho_7 = 0.041$ $\rho_8 = 0.006$ $\rho_9 = \rho_{10} = -0.003$ $\rho_{11} = 0.004$	0.167
H	β-CH_3	$\rho_1 = \rho_5 = 0.046$ $\rho_2 = \rho_4 = 0\ 012$ $\rho_3 = 0.120$ $\rho_6 = 0.092$	$\rho_7 = 0.025$ $\rho_8 = \rho_{11} = 0\ 003$ $\rho_9 = \rho_{10} = -0.001$	0.203
o-CH_3	H	$\rho_1 = 0\ 013$ $\rho_2 = \rho_4 = 0.021$ $\rho_3 = 0.023$ $\rho_5 = 0.013$ $\rho_6 = 0.081$	$\rho_7 = 0\ 021$ $\rho_8 = \rho_{11} = 0.006$ $\rho_9 = \rho_{10} = -0.002$	0.261
p-CH_3	H	$\rho_1 = \rho_5 = 0.032$ $\rho_2 = \rho_4 = 0.021$ $\rho_3 = 0.002$ $\rho_6 = 0.125$	$\rho_7 = 0.021$ $\rho_8 = \rho_{11} = 0.006$ $\rho_9 = \rho_{10} = -0.002$	0.261
o-CH_3	α-CH_3	$\rho_1 = 0.013$ $\rho_2 = \rho_4 = 0.021$ $\rho_3 = 0.023$ $\rho_5 = 0\ 013$ $\rho_6 = 0.081$	$\rho_7 = 0.02$ $\rho_8 = \rho_{11} = 0.004$ $\rho_9 = \rho_{10} = -0.003$	0.326
p-CH_3	α-CH_3	$\rho_1 = \rho_5 = 0.032$ $\rho_2 = \rho_4 = 0.021$ $\rho_3 = 0.102$ $\rho_6 = 0.125$	$\rho_7 = 0.021$ $\rho_8 = \rho_{11} = 0\ 006$ $\rho_9 = \rho_{10} = -0.002$ $\rho_9 = \rho_{10} = -0.002$	0 241
p-CH_3	β-CH_3	$\rho_1 = \rho_5 = 0.032$ $\rho_2 = \rho_4 = 0.021$ $\rho_3 = 0.102$ $\rho_6 = 0.125$	$\rho_7 = 0.021$ $\rho_8 = \rho_{11} = 0.004$ $\rho_9 = \rho_{10} = -0.001$	0.262
m-CH_3	H	$\rho_1 = \rho_5 = 0.055$ $\rho_2 = 0.029$ $\rho_3 = 0.003$ $\rho_4 = 0.024$ $\rho_6 = 0.118$	$\rho_7 = 0.027$ $\rho_8 = \rho_{11} = 0.007$ $\rho_9 = \rho_{10} = 0.002$	0 258

[a] The numbering scheme is shown in Fig. 1.

substantiate this is obtained by replacing all the hydrogen atoms of the phenyl ring by deuterium atoms. It is observed that $C_6D_5COC_5H_4Mn(CO)_3$ gives just the six ^{55}Mn hyperfine lines, (width 2.5 G) but no other resolvable hyperfine structure under similar conditions. This suggests that the splittings from the cyclopentadienyl protons are small which is consistent with theoretical predictions. A methyl group at the β-position of the Cp ring has little effect on the splittings. However, when it is at the α position, the effect is quite significant. One sees a

TABLE 3

COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED SPIN DENSITIES FOR $C_6H_4RCOC_5H_3R'Mn(CO)_3^-$

Experimental					Theoretical		
R	R'	$\rho(Mn)$	$\rho(p)^b$	$\rho(o)^c$	$\rho(Mn)$	$\rho(p)$	$\rho(o)$
H	H	0.203	0.122	0.044	0.200	0.120	0.052
H	α-CH_3	0.163	0.145	0.036	0.167	0.134	0.042
H	β-CH_3	0.205	0.126	0.044	0.203	0.120	0.046
o-CH_3	H	0.312	0.012	0.008	0.326	0.023	0.013
p-CH_3	H	0.238	<0.012	<0.008	0.261	0.002	0.032
o-CH_3	α-CH_3	0.316	<0.025	<0.020	0.326	0.023	0.013
p-CH_3	α-CH_3	0.204	<0.108	<0.037	0.241	0.102	0.032
p-CH_3	β-CH_3	0.239	<0.100	<0.020	0.262	0.102	0.032

[a] The values of densities at *meta* positions are not given since hyperfine structures due to the *meta* protons are not observed for any of these radicals. [b] *Para* position (Fig. 1, position 3). [c] *Ortho* position (Fig. 1, positions 1 and 5).

lowering in A(Mn) with an increase in A(*p*-H). This is consistent with an increase in spin density on the phenyl and a decrease on the Mn. This is expected on electronic grounds as the CH_3 donates electrons onto the Cp ring and most likely onto the manganese and thus makes it less favorable for spin density. There might also be some steric effect. Space filling models show no significant steric hindrance when the unsubstituted ligand is completely planar. With a β-methyl or a *m*- or *p*-methyl, there is no increase in steric hindrance in this configuration. With an α-methyl, there is some slight steric hindrance and so the Cp ring might twist a little out of the plane of the ketonic CO group. This would mean an increase in spin density on phenyl and a decrease on the $CpMn(CO)_3$ group and this would be consistent with the observed spectra. If there is a CH_3 at the *o*-position, there is substantial steric hindrance in the planar configuration and so the phenyl ring cannot be in the plane of the ketonic CO. The spectral results are in agreement with this as there is a large increase in A(Mn) when there is an *o*-methyl substituent. Unfortunately, no proton splittings were observed. It seems that if there is sufficient spin density on the Mn to cause an A(Mn) of 7.9×10^{-4} cm^{-1} or greater then one has too little spin density on the phenyl to observe phenyl proton splittings with the sort of resolution obtainable. This increase in A(Mn) with *o*-substitution is also in agreement with the expected electronic trends outlined above.

The results for the *m*- and *p*-substituted derivatives are also in agreement with the above arguments. Some of the *p*-methyl derivatives show CH_3 proton splittings in addition to those of the ring protons.

The total spin densities on carbon and manganese atoms are reported in Table 2. In all these calculations the carbon skeleton of the organic ligand is assumed to be planar with the ketonic oxygen in the plane of the two rings. Calculations with a non-planar carbon skeleton could not be reconciled with the recorded spectra. Either the ratio of triplet to doublet spin densities was 2.4 times the experimental value or an additional triplet splitting was predicted which was not observed experimentally.

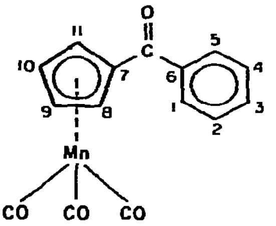

Fig. 1. Numbering scheme used in the description of spin densities of benzoylcyclopentadienylmanganese tricarbonyl anion.

The calculations show that in all the anion radicals studied here the largest density (ρ(CO) = 0.39-0.52) is on the ketonic group. A similar observation was made in the case of ferrocene radicals [14, 15]. The density on the cyclopentadienyl ring is small and a significant density is found on the metal. These calculations clearly show that the radicals are essentially of the π-type. The existence of negative densities cannot be predicted since in all these calculations the electron correlation is neglected so a perturbation calculation was carried out using McLachlan's method [16]. These calculations predict a small negative density at two sites on the cyclopentadienyl ring. The results of these calculations are summarised in Table 2. The numbering scheme is shown in Fig. 1. In order to translate the spin densities into proton hyperfine coupling constants or vice versa, a knowledge of the Q(H) value is needed. Since the value of Q is not known in the present case, the data is fitted to the equation $A = Q(\mathrm{H})\rho$. A value of $Q(\mathrm{H}) = -24$ G is found to give the best fit. This is very close to the value observed for other ring systems [17] lending credence to the calculations. A similar fit for Mn gives a value of 38 G for Q(Mn), i.e., $A(\mathrm{Mn}) = 38\,\rho(\mathrm{Mn})$.

A comparison of experimental and calculated values of hyperfine constants is given in Table 3. The agreement is good in view of the complexity and number of approximations made in arriving at the calculated values. This is interesting in view of the qualitative arguments given above on the basis of electronic and steric effects, for it means that steric hindrance plays only a minor role. Therefore the predominant effect of the substituents is electronic in nature.

The g values for all the radicals reported here are smaller than the free electron g value which suggests a significant spin orbit coupling. This is consistent with our experimental observation of a relatively short and temperature-dependent relaxation time and considerable g-anisotropy observed at low temperature. These results indicate major participation of metal $3d$ and $4p$ orbitals in agreement with our MO calculations.

These findings also demonstrate that there is extensive electron delocalization over the entire system with the density predominately centred on the phenyl ring, the ketonic CO and the Mn atom.

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