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Relationships between Ligand Carbon-13 Chemical Shifts and Reduction Potentials of Mn(III) Complexes

W. M. COLEMAN

Naval Biosciences Laboratory, University of California, Berkeley Naval Supply Center, Oakland, Calif. 94625, U.S.A.

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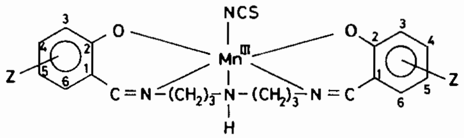
We have been interested in the reactivity patterns of certain manganese complexes toward dioxygen and nitric oxide [1–6] and have observed dramatic effects on the reactivity patterns as a function of substitution (Z) on the complexing ligand (Structure I). Studies employing cyclic voltammetry have been undertaken to determine if these reactivity patterns could be related to the electrochemical properties of the complexes [7, 8]. It was found that those complexes with electron withdrawing substituents (–NO_2, –Br, –Cl) had reduction potentials (Ep) much more positive than those with electron donating groups (–OCH_3, –H, –CH_3). It was easier to reduce Mn(III) to Mn(II) in those complexes with electron withdrawing groups.



In those papers we postulated that substituent effects were transmitted through the π electron system of the ligand to the metal ion itself. We wish to present our results obtained by means of ^{13}C NMR in an effort to support this contention.

Experimental

The 3- and 5-nitrosalicylaldehyde were obtained from Eastman Chemical Company. The following chemicals were obtained from Aldrich, 2-hydroxy-1-naphthaldehyde, 5-methyl-2-hydroxyacetophenone and 5-methyl-2-hydroxybenzophenone and were used as received. Salicylaldehyde, 3-methoxysalicylaldehyde, 5-methoxysalicylaldehyde, 2-hydroxyacetophenone and 2-hydroxybenzophenone were distilled *in vacuo* prior to use. 5-Bromosalicylaldehyde and 5-methylsalicylaldehyde were synthesized by a method described previously [9]. 5-Nitro-2-hydroxybenzophenone was synthesized by reducing the corresponding acid chloride [10]. 5-Bromo-2-hydroxyacetophenone was synthesized by the method of Lavit [11].

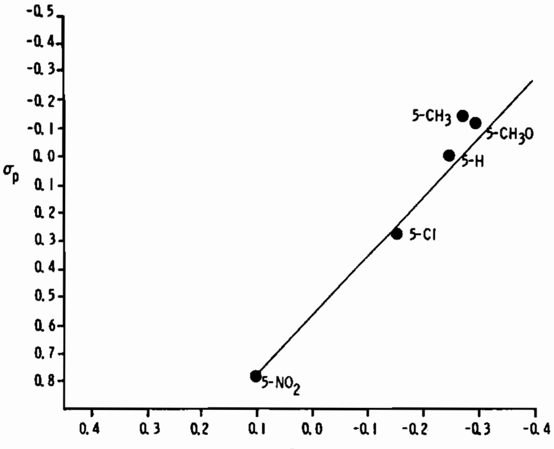


Fig. 1, Plot of σp values for substituents *versus* the reduction potential for the corresponding Mn(III) complex. The line is drawn from a linear regression analysis.

Carbon-13 NMR spectra were obtained on a Varian Model FT80A Spectrometer employing 10 mm sample tubes and $CDCl_3$ as solvent. All chemical shifts are cited from internal TMS. No significant chemical shifts were noted as a function of concentration. Approximately 500 scans were obtained on each sample.

Results and Discussion

The set of numerical values derived from the Hammett equation serve as a basic source for quantitative treatments of the effect of structure on reactivity [12]. The σ factor or values from the Hammett equation are numbers which sum up the total electrical effects (resonance and inductive) of a group X when attached to a benzene ring in the *para* and *meta* positions relative to group Y. The electrochemical reduction potentials (Ep) for a set of Mn(III) complexes were found to be related to Hammett σ vaues graphically displayed in Fig. 1. Linear regression analysis yielded a correlation coefficient of 0.9931 between the reduction potentials (Ep) and the Hammett values. Consequently it was concluded that these substituents are indeed exerting electrical effects on the Mn(III) ion. If these effects are transmitted through the aromatic π electron network, the chemical shift of the aromatic carbons must be affected. Indeed, such a relationship between

TABLE 1. Pertinent Data on ^{13}C Chemical Shifts, Hammett σ values, and MnIII Reduction Potentials.

Compound	σ_p	δ C–O	MnIII E_p
H-SAL[a]	0	161.57 (161.40)[e]	−0.245
5-CH_3SAL	−0.13	159.59	−0.272
3-CH_3OSAL		151.53	−0.279
5-CH_3OSAL	−0.11	155.92	−0.290
NAP[b]		164.78	−0.303
5-BrSAL	0.27	160.57	−0.150
5-ClSAL		160.50	
3-NO_3SAL		156.60	+0.025
5-NO_2SAL	0.78	166.19	+0.110
H-HAP[c]		162.42 (162.30)[e]	
5-Br-HAP		161.14	
5-CH_3HAP		160.37	
H-HBP[d]		163.31	
5-NO_2HBP		168.03	
5-CH_3HBP		161.27	

[a] SAL = salicylaldehyde. [b] NAP = 2-hydroxyl-1-naphthaldehyde. [c] HAP = 2-hydroxyacetophenone. [d] HBP = 2-hydroxybenzophenone. [e] See (14).

Hammett σp values and ^{13}C chemical shifts has been shown to exist in monosubstituted benzenes [13]. In summary, those groups with high σp values (–NO_2) produced the most deshielded para carbons. Thus, the ^{13}C chemical shift of the carbon with the phenolic oxygen attached should be a function of the para substituent (position 5). Table I shows the results obtained from the ^{13}C NMR experiments. In Fig. 2A these observed chemical shifts are plotted *versus* the corresponding σ values according to Stothers [13].

We attempted to compare the phenoxy carbon chemical shifts with the comparable Mn(III) complex's reduction potential (Ep). The results of such a comparison are shown in Fig. 2B. For those groups bound to position 5, one can see a sequence traversing from the most deshielded 5-NO_2 case to the least deshielded 5-CH_3O case accompanied by a comparable shift to more negative reduction potentials. In addition to the para substituted compounds (position 5) shown on the graph, the 3- or ortho substituted positions are cited. Both the 3-NO_2 and 3-CH_3O groups at least follow the same general trend even though steric effects are known to be present in the ortho cases.

In an attempt to mathematically describe the Mn(III) reduction potential (Ep) chemical shift relationship depicted in Fig. 2B a linear regression analysis was performed on the data points for the para substituted cases (position 5). The equation that subsequently evolved is shown below:

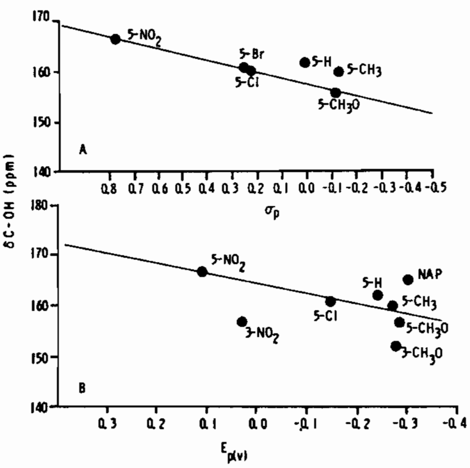


Fig. 2. Plot of phenoxy carbon chemical shift *versus* the corresponding σp value (A). Plot of phenoxy carbon chemical shifts *versus* the corresponding Mn(III) reduction potential (B).

$$\delta C\text{–}O = 19.726\,(Ep) + 164.096$$

The line drawn in Fig. 2B is derived from the equation. The correlation coefficient for the five points was found to be 0.879. For 5% confidence level the required value for a correlation coefficient is 0.878 [15].

In summary, ligand ^{13}C NMR data (δC) have been shown to correlate with the reduction potential of the comparable Mn(III) complex (Ep). The data is significant in that it clearly supports the postulates advanced in preceding papers concerning the transmission of electronic effects through the aromatic π electron network to a Mn(III) ion.

Acknowledgement

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15 Equation was derived from a manual for Texas Instrument Calculators 58/59 entitled Applied Statistics, pp 5 - 6, Published by Texas Instruments, 1977, Dallas, Tex.