

Transmission of Substituent Effects in Phenoltricarboxylchromium Compounds

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The acidities of several substituted phenoltricarboxylchromium compounds have been determined in 50% ethanol. A plot of pK_a values versus Hammett substituent constants indicates that no distortion of substituent effects occurs upon complexation of an aromatic system to the tricarboxylchromium moiety.

THE manner in which the tricarboxylchromium group affects the arene ligand in arenetricarboxylchromium complexes is of much theoretical interest.^{1,2} The X-ray structural analysis of benzenetricarboxylchromium³ reveals no significant structural modifications of the benzene ring; however, the chemical properties of arenes have been shown to be greatly altered upon coordination to chromium. For example, anilinetri-carboxylchromium is a weaker base than aniline and complexed benzoic acid is a stronger acid than un-complexed benzoic acid.^{4,5} Chlorobenzenetricarboxyl-chromium undergoes nucleophilic substitution at room temperature whereas the free arene does not.^{5,6} Solvolysis rates of (benzyl chloride)tricarboxylchromium and

(benzhydryl chloride)tricarboxylchromium indicate that the complexed compounds solvolyse faster than the uncomplexed compounds by factors of 10^5 and 10^3 respectively.⁷

Since the reactivity of the benzene ring is clearly affected by its interaction with the tricarboxylchromium group, investigations were undertaken to determine the ability of a benzene ring to transmit substituent effects through its co-ordinated π -electron system. After studying the hydrolyses of several tricarboxylchromium complexes of substituted benzoic acid esters, Klopman and Calderazzo concluded that an aromatic system bonded to a $Cr(CO)_3$ group showed a dependence of reactivity on structure very similar to that of an un-complexed aromatic system.⁸ Interestingly, a study of

¹ S. P. Gubin and V. S. Khandkarova, *J. Organometallic Chem.*, 1970, **22**, 449.

² V. S. Khandkarova, S. P. Gubin, and B. A. Kvasov, *J. Organometallic Chem.*, 1970, **23**, 509.

³ M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1314.

⁴ E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, and W. Semmlinger, *Chem. Ber.*, 1958, **91**, 2763.

⁵ B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 1959, 551.

⁶ D. A. Brown and J. R. Raju, *J. Chem. Soc. (A)*, 1966, 1617.

⁷ J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometallic Chem.*, 1965, **4**, 324.

⁸ G. Klopman and F. Calderazzo, *Inorg. Chem.*, 1967, **6**, 977.

the thermodynamic stabilities of several substituted benzyltricarboxylchromium cations⁹ showed a much better correlation with Hammett σ values than with σ^+ . This is in contrast to stabilities of uncomplexed benzyl carbonium ion systems which correlate with σ^+ (indicating direct resonance interactions between substituents and reaction centres).¹⁰ This led to the suggestion that the interaction of the aromatic system with the carbonium ion in the complexed cation is much different from that found in the free cation.⁹ Since recent theoretical studies indicate that very little change should occur in the π -electron character of the ring upon complex formation,^{1,2} study was begun with other systems in which direct resonance interactions between substituents could occur through the co-ordinated π -electron system. Recent investigations of the n.m.r. spectra of several substituted anilinetricarbonylchromium compounds indicated that shielding of the protons attached to the nitrogen (+R) group was greatly modified by a strong direct resonance interaction with a -R substituent in the *para*-position.¹¹ Since similar results are obtained in the uncomplexed system, the co-ordinated π -electron system appeared to function normally in resonance interactions. This result is in apparent contrast to the previous observations of Trahanovsky *et al.*⁹ The present study was then undertaken to determine whether this behaviour is found in other similar systems.

EXPERIMENTAL

Microanalyses were performed by Chemalytics, Inc., Tempe, Arizona. I.r. spectra were obtained with a Perkin-Elmer model 457 spectrophotometer, with chloroform as solvent and polystyrene as the reference standard. M.p.s (or decomposition points) were determined in sealed capillaries under nitrogen and are uncorrected.

The tricarbonylchromium complexes of phenol,⁴ *p*-cresol,¹² *m*- and *p*-hydroxyacetophenone¹³ were prepared and purified according to literature procedures.

(*Methyl p-Hydroxybenzoate*)tricarbonylchromium.—Hexacarbonylchromium (3 g) and methyl *p*-hydroxybenzoate (3 g) were dissolved in butyl ether (50 ml) and refluxed under nitrogen for 6 h with manual return of sublimed hexacarbonylchromium. The solvent was removed *in vacuo*. The residue was recrystallized from benzene–light petroleum to yield the desired compound as bright yellow needles (2.4 g, 61%), m.p. 118–120° (decomp.). The metal carbonyl i.r. absorption bands were observed at 1975 and 1900 cm^{-1} (Found: C, 45.95; H, 2.65. Calc. for $\text{C}_{11}\text{H}_8\text{CrO}_6$: C, 45.85; H, 2.8%).

(*Methyl m-Hydroxybenzoate*)tricarbonylchromium.—Three grams each of $\text{Cr}(\text{CO})_6$ and methyl *m*-hydroxybenzoate were treated as above. After removal of the solvent, the residue was chromatographed over silica. Elution with benzene removed a green band which was discarded. Benzene–ether (1 : 1 v/v) eluted an orange band. Removal

⁹ W. S. Trahanovsky and D. K. Wells, *J. Amer. Chem. Soc.*, 1969, **91**, 5870.

¹⁰ H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

¹¹ Angela Wu, E. R. Biehl, and P. C. Reeves, *J. Organometallic Chem.*, 1971, **33**, 53.

of the solvent and recrystallization from benzene–light petroleum afforded the desired compound as orange-red crystals (1.2 g, 30%), m.p. 135–137° (Found: C, 45.65; H, 2.75. Calc. for $\text{C}_{11}\text{H}_8\text{CrO}_6$: C, 45.85; H, 2.8%).

pK_a Measurements.—All *pK_a* measurements were conducted in 50% ethanol solutions by titrimetric methods at $20 \pm 1^\circ\text{C}$. Solvents were degassed and nitrogen was bubbled through the solutions during the titrations. A Beckman Zeromatic pH meter and glass electrode were used. Standardization was accomplished by the use of an aqueous ethanol buffer.¹⁴

The weighed compound (0.5 mmol) was first dissolved in absolute ethanol (22.5 ml) and then distilled water (22.5 ml) was added. During the titration, equal amounts (0.5 ml) of 0.1N-NaOH and ethanol were added, and the pH values thus obtained were used to calculate the *pK_a* values by the method of Albert and Serjeant.¹⁵ The *pK_a* values of the substituted phenols, both complexed and uncomplexed, are listed in the Table.

pK Values of substituted phenols and substituted phenol-tricarboxylchromium complexes in 50% ethanol

Substituent	Uncomplexed	Complexed
<i>p</i> -Me	11.28	7.32
<i>p</i> -H	11.02	7.09
<i>m</i> -CO ₂ Me	10.05	6.77
<i>m</i> -Ac	9.99	6.82
<i>p</i> -CO ₂ Me	9.17	6.40
<i>p</i> -Ac	8.81	6.31

RESULTS AND DISCUSSION

The *pK_a* values of a series of substituted phenol-tricarboxylchromium complexes have been determined in 50% ethanol. The results (Table) show that these complexed phenols are much stronger acids than the corresponding uncomplexed phenols. This increased acidity is most likely due to the strong electron-withdrawing property of the $\text{Cr}(\text{CO})_3$ system which stabilizes the phenoxide ion. The transmission of electronic effects from the substituent to the reaction centre can be clearly seen (Figure 1). A very good correlation is obtained when *pK_a* is plotted *versus* Hammett σ^- values for *p*-CO₂Me and *p*-Ac (plot B). As can be seen a significantly poorer correlation would be obtained if the normal σ values for these substituents were used. This is significant in that these two substituents (-R groups) are capable of direct resonance interaction with the phenoxide oxygen (+R group). As seen in plot A (Figure 1), a similar correlation is obtained with the uncomplexed phenols. These results seem to be quite different than those obtained by Trahanovsky in the case of the complexed benzyl cations.⁹

From Figure 1, it can be seen that the slope of the plot for the uncomplexed compounds (2.51) is greater than that of the complexed compounds (0.99). A similar result has been observed in previous studies^{8,11} and simply indicates that the complexed phenols are less

¹² H. P. Fritz and C. G. Kreiter, *J. Organometallic Chem.*, 1967, **7**, 427.

¹³ J. Besancon and J. Tirouflet, *Rev. Chim. min.*, 1968, **5**, 363.

¹⁴ R. G. Bates, 'Determination of pH,' Wiley, New York, 1964, p. 227.

¹⁵ A. Albert and E. P. Serjeant, 'Ionization Constants of Acids and Bases,' Wiley, New York, 1962, p. 36.

sensitive to electronic changes in the aromatic ring induced by the substituents. The strongly electron-withdrawing tricarbonylchromium group induces a considerable effective positive charge on the complexed aromatic system. This decreased electron density would diminish any effect caused by the donation of electron density by a substituent and would act against any further removal of electron density by a substituent.

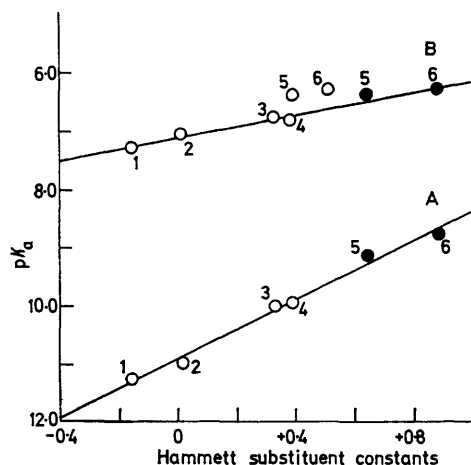


FIGURE 1 Plot of pK_a versus Hammett substituent constants: \circ Hammett σ value; \bullet σ^- value; (A) uncomplexed, (B) complexed compounds. (1) *p*-Me, (2) *p*-H, (3) *m*-CO₂Me, (4) *m*-Ac, (5) *p*-CO₂Me, (6) *p*-Ac

In Figure 2, pK_a values for the uncomplexed phenols are plotted versus pK_a values for the complexed phenols. The two sets of pK_a values are observed to be linearly related for all substituents studied. Since no serious

deviation from linearity is found, it can be concluded that no distortion of substituent effects occurs upon

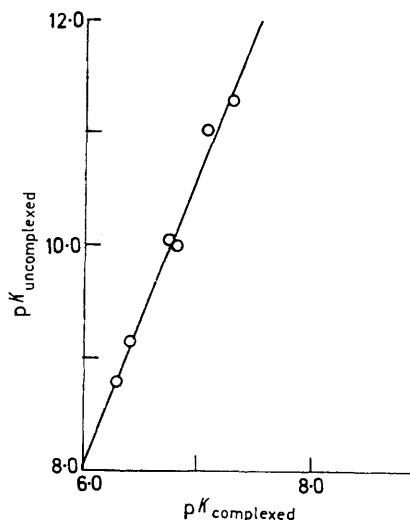


FIGURE 2 Plot of pK_a values for uncomplexed phenols versus pK_a values for complexed phenols: (1) *p*-Me, (2) *p*-H, (3) *m*-CO₂Me, (4) *m*-Ac, (5) *p*-CO₂Me, (6) *p*-Ac

complex formation of an aromatic system to the tricarbonylchromium group. However, the electronic transmission is slightly suppressed by the buffering action of the strongly electron-withdrawing Cr(CO)₃ group.

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