Voltammetric Oxidation of Arene, Cycloheptatriene, and Cycloheptatrienyl Tricarbonyl Complexes of Chromium

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The series of π-arene chromium tricarbonyl complexes $[(\pi\text{-}C_6H_nMe_{6-n})Cr(CO)_3]$ (*n* = 0—6), $[(\pi\text{-}C_6H_5R)Cr(CO)_3]$ (R = Pr^i, NH_2, NHMe, NMe_2, OMe, CO_2Me, and Cl), and $[(\pi\text{-}C_6H_4RR')Cr(CO)_3]$ (R = Me, R' = Pr^i; R = Me, R' = NH_2) undergo, voltammetrically, two one-electron oxidation processes. The $E_{\frac{1}{2}}$-value for the oxidation waves are dependent on the nature of the arene ring substituents but are independent of ring substituent positional isomerism. There is a linear correlation between $E_{\frac{1}{2}}$ (complex) and $E_{\frac{1}{2}}$ (free arene), and between $E_{\frac{1}{2}}$ (complex) and the ionisation potentials of the complexes $[(\pi\text{-}C_6H_nMe_{6-n})Cr(CO)_3]$ and of the free arenes. The cycloheptatriene species $[(\pi\text{-}C_7H_6RR')Cr(CO)_3]$ (R = H, R' = H, *exo*- or *endo*-Ph, and *exo*-CN; R = R' = OMe) may also be oxidised to $[(\pi\text{-}C_7H_6RR')Cr(CO)_3]^+$ and the species where R = H, R' = exo-CN and R = R' = OMe may be reduced in a one-electron step. The cycloheptatrienyl complexes $[(\pi\text{-}C_7H_7R)Cr(CO)_3]^+$ (R = H or OMe), undergo an irreversible one-electron reduction process.

IN our previous paper,[1] we have shown that $[M(CO)_{6-n}L_n]$, where L = tertiary phosphine, amine, isocyanide, or carbene (CXY), underwent a reversible, or quasi-reversible, one-electron voltammetric oxidation process. The half-wave potential for the general reaction (1) is dependent on the nature of M, *n*, and the π-acceptor/σ-donor properties of L.

$$[M(CO)_{6-n}L_n]^0 \rightleftharpoons [M(CO)_{6-n}L_n]^+ + e^- \quad (1)$$

It has been established that, in acetonitrile, $(\pi\text{-}C_6H_6)\text{-}Cr(CO)_3$ undergoes,[2] voltammetrically, a one-electron oxidation and that ferrocenyl-substituted arene chromium tricarbonyl derivatives behave similarly. The data suggest that the ferrocenyl group is electron-withdrawing.

In order to define more clearly the substituent effects on the voltammetric properties of arene chromium carbonyls, and to establish whether closely related (conjugated) triolefinic species could be similarly oxidised, we have studied the voltammetric oxidation of substituted benzene, cycloheptatriene, and cycloheptatrienyl chromium tricarbonyl complexes.

RESULTS

The voltammetric studies were carried out in dichloromethane using a rotating platinum electrode. The voltammograms of the substituted benzene complexes exhibited two oxidation waves, whereas the cycloheptatriene derivatives exhibited only one oxidation process, and, in two cases, one reduction wave. The cationic cycloheptatriene compounds displayed one reduction wave.

The Species $[(\pi\text{-arene})Cr(CO)_3]$: *Alkyl-substituted Benzene Complexes.*—The voltammograms obtained from the methyl- and isopropyl-substituted benzene chromium tricarbonyl complexes were well defined and exhibited two one-electron oxidation process, $E_{\frac{1}{2}}$ (I) and $E_{\frac{1}{2}}$ (II) (Table 1). The addition of a methyl group to the benzene ring of $[(\pi\text{-}C_6H_6)Cr(CO)_3]$ caused a reduction of 30 mV in the value of $E_{\frac{1}{2}}$(I) relative to that of the parent species, and further substitution on the aryl ring of H by Me caused the oxidation potential to decrease still further. Significantly, there was no substantial ring positional effect on $E_{\frac{1}{2}}$(I). The $E_{\frac{1}{2}}$(I)-value of $[(\pi\text{-cumene})Cr(CO)_3]$ was predictably lower than that of $[(\pi\text{-toluene})Cr(CO)_3]$.

The second oxidation wave was difficult to observe because of electrode coating. While there was no regular substituent effect on $E_{\frac{1}{2}}$(II), the more highly substituted species had more cathodic potentials than those of their less substituted analogues.

TABLE 1

$E_{\frac{1}{2}}$-Data obtained from alkyl-substituted arene chromium tricarbonyl complexes, $[(\pi\text{-arene})Cr(CO)_3]$

Arene	$E_{\frac{1}{2}}$(I) [a]	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ [b]	i_d/c [c]	$E_{\frac{1}{2}}$(II) [d]	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ [b]	i_d/c [c]
C_6H_6	0·71	57	3·6	1·80	80	
C_6H_5Me	0·68	55	3·5	1·53	76	
o-$C_6H_4Me_2$	0·64	75	3·1	1·73	66	
m-$C_6H_4Me_2$	0·64	75	3·3	1·72	67	
p-$C_6H_5Me_2$	0·64	68		1·76	74	
1,3,5-$C_6H_3Me_3$	0·58	71	3·0	1·77	74	
1,2,4,5-$C_6H_2Me_4$	0·60	60	5·5	1·43	67	6·4
C_6HMe_5	0·60	66	5·8	1·14	87	4·9
C_6Me_6	0·55	61	5·3	1·11	85	5·5
C_6H_5(Pr^i)	0·67	69	5·4	1·23	85	5·8
p-C_6H_4Me(Pr^i)	0·66	59	5·0	1·45	80	5·4

[a] First oxidation potential, in V, *versus* S.C.E. in CH_2Cl_2. [b] Reversibility criterion; for a reversible one-electron process, $E_{\frac{3}{4}} - E_{\frac{1}{4}} = 59$ mV. [c] In μA mmol^{-1}; for a one electron process using the cell in this series of experiments, $i_d/c = 3{\cdot}5$ or 5·0 depending on Pt electrode (data established using $[Ni\{S_2C_2(CN)_2\}_2]^{2-}$). [d] Second oxidation potential; for 1st and 2nd oxidation, cyclic voltammetry established both processes accompanied by coupled chemical reactions.

Other Substituted Benzene Complexes.—The values of $E_{\frac{1}{2}}$(I) for the aniline and *N*-methyl substituted aniline complexes are at least 270 mV more cathodic than the potential obtained from $[(\pi\text{-}C_6H_6)Cr(CO)_3]$ (Table 2). Again, positional isomerism had no effect on the $E_{\frac{1}{2}}$-value. Methylation of the amino-group in $[(\pi\text{-}C_6H_5NH_2)Cr(CO)_3]$ had the effect of lowering the value of $E_{\frac{1}{2}}$(I) relative to that of the aniline complex. The π-anisole complex had an $E_{\frac{1}{2}}$-value identical to that of $[(\pi\text{-}C_6H_6)Cr(CO)_3]$ while the oxidation potential for $[(\pi\text{-}C_6H_5CO_2Me)Cr(CO)_3]$ was more anodic. The complex $[(\pi\text{-}C_6H_5Cl)Cr(CO)_3]$ showed an oxidation wave at about +0·70 V but, because of electrode coating, the wave height was severely diminished. Attempts to study the oxidation behaviour of $[(\pi\text{-}C_6H_6)W(CO)_3]$ were also hindered by electrode coating.

The value of $E_{\frac{1}{2}}$(II) in these complexes was little in-

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[1] M. K. Lloyd, J. A. McCleverty, D. G. Orchard, J. A. Connor, M. B. Hall, I. M. Hillier, E. M. Jones, and G. K. McEwen, *J.C.S. Dalton*, **1973**, 1743.

[2] S. P. Gubin and V. S. Khandkarova, *J. Organometallic Chem.*, 1970, **22**, 449.

fluenced by substituents, and failure to observe a second wave in $[(\pi\text{-}C_6H_5OMe)Cr(CO)_3]$ and $[(\pi\text{-}C_6H_5CO_2Me)Cr(CO)_3]$ can be attributed to its probable occurrence at a potential greater than that of the oxidation of the solvent–base electrolyte medium (*ca.* +1·6 V).

TABLE 2

$E_{\frac{1}{2}}$-Data obtained from other π-arene chromium tricarbonyl complexes

Arene	$E_{\frac{1}{2}}(I)$ [a]	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$	i_d/c	$E_{\frac{1}{2}}(II)$	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$
$C_6H_5NH_2$	0·44	80	3·5	1·34	69
o-$C_6H_4Me(NH_2)$	0·40	73	3·7	1·52	65
m-$C_6H_4Me(NH_2)$	0·41	73			
p-$C_6H_4Me(NH_2)$	0·40	80	3·2	1·55	61
$C_6H_5(NHMe)$	0·36	85	3·4	1·52	87
$C_6H_5NMe_2$	0·36	75		1·45	60
C_6H_5OMe	0·71	70	3·0	1·65	56
$C_6H_5CO_2Me$	0·80	65	3·3		
C_6H_5Cl	*ca.* 0·7				

[a] Data as in Table 1.

DISCUSSION

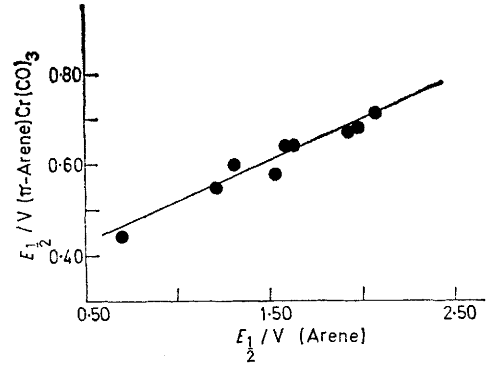
Miller *et al.*[3] have recently measured the oxidation potentials of a wide variety of arenes (in MeCN using a Pt electrode *vs.* a Ag/Ag$^+$ reference cell) and have shown that there is a linear relationship between $E_{\frac{1}{2}}$ (arene) and the ionisation potential (I) of the free hydrocarbon.

TABLE 3

$E_{\frac{1}{2}}$-Data obtained from cycloheptatriene and cycloheptatrienyl chromium tricarbonyl complexes

Complex	$E_{\frac{1}{2}}$ [a]	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$	i_d/c	$E_{\frac{1}{2}}$ [b]	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$	i_d/c
$[(\pi\text{-}C_7H_8)Cr(CO)_3]$	0·67	109				
$[\{\pi\text{-}C_7H_7(\text{endo-Ph})\}Cr(CO)_3]$	0·62	74	5·6			
$[\{\pi\text{-}C_7H_7(\text{exo-Ph})\}Cr(CO)_3]$	0·69	70				
$[\{\pi\text{-}C_7H_7(\text{exo-CN})\}Cr(CO)_3]$	0·77	57	4·7	−0·26	160	4·2
$[\{\pi\text{-}C_7H_6(OMe)_2\}Cr(CO)_3]$	1·03	100	4·8	−0·27	175	6·2
$[(C_7H_6O)Cr(CO)_3]$ [c,d]	0·95	80	4·8			
$[(\pi\text{-}C_7H_7)Cr(CO)_3]^+$ [d]				−0·72	105	
$[\{\pi\text{-}C_7H_6(OMe)\}CrCO)_3]^+$ [d]				−0·23	70	4·7

[a] Oxidation potential, data as in Table 1. [b] Reduction potential. [c] Tropone complex. [d] As PF_6^- salt.



$E_{\frac{1}{2}}(I)$ plotted against $E_{\frac{1}{2}}$ (free arene)

We have found a linear correlation between $E_{\frac{1}{2}}(I)$ for the arene metal complexes and both $E_{\frac{1}{2}}$ and I for the free arene. The slope of the graph obtained by plotting $E_{\frac{1}{2}}(I)$ *vs.* $E_{\frac{1}{2}}$ (free arene) (Figure) reveals that $E_{\frac{1}{2}}(I)$ is less sensitive to changes in arene substituent than is $E_{\frac{1}{2}}$ for the oxidation of the free arene. This may indicate that the complex cation is more stabilised by solvation than is the free ligand cation.

There is also a linear relationship between $E_{\frac{1}{2}}(I)$ and I for the metal complexes[4] (slope 0·5) and I for the free ligand (slope 0·62) containing alkyl substituents; the correlations are less good for the species containing $C_6H_5NH_2$, $C_6H_5NMe_2$, C_6H_5Cl, and $C_6H_5CO_2Me$. These linear relationships indicate that the redox orbital in the arene chromium tricarbonyl complexes is strongly influenced by the arene ligand. We are unable, however, to demonstrate unambiguously that the redox orbital is arene ligand-based.[1]

Cycloheptatriene and Cycloheptatrienyl Chromium Tricarbonyl Species.—The cycloheptatriene complexes exhibited an oxidation wave (Table 3) between +0·65 and +1·03 V, and two complexes had a reduction wave at *ca.* −0·26 V. The $E_{\frac{1}{2}}$-value of $[(\pi\text{-}C_7H_8)Cr(CO)_3]$ was very similar to that of its isomer $[(\pi\text{-}C_6H_5Me)Cr(CO)_3]$.

Substitution of the *exo*-methylene proton in $[(\pi\text{-}C_7H_8)Cr(CO)_3]$ by Ph or CN caused the $E_{\frac{1}{2}}$-value for the oxidation to increase by 20 and 100 mV respectively. Remarkably, however, the $E_{\frac{1}{2}}$-value for the *endo*-phenylcycloheptatriene complex was 50 mV *lower* than that of the parent species, and 70 mV *lower* than that of its *exo*-isomer. Thus positional isomerism at the methylene carbon atom alters significantly the ease with which an electron can be removed from this particular system. Although the molecular structure of the *exo*-isomer has been determined,[5] that of the *endo*-form has not. So, in the absence of definitive structural information, we can only speculate that steric factors have an important bearing on the redox properties of these isomers.

The complex $[\{\pi\text{-}C_7H_6(OMe)_2\}Cr(CO)_3]$ had the highest $E_{\frac{1}{2}}$-values of this series of compound, and this was unexpected in view of the results obtained from $[(\pi\text{-}C_6H_5OMe)Cr(CO)_3]$. Both $[(\pi\text{-}C_7H_7CN)Cr(CO)_3]$ and $[\{\pi\text{-}C_7H_6(OMe)_2\}Cr(CO)_3]$ exhibited reduction waves, at −0·26 and −0·27 V respectively. None of the other complexes underwent reduction behaviour in dichloromethane, although, in 1,2-dimethoxyethane, Dessy and

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[3] L. L. Miller, G. D. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, 1972, **37**, 916.

[4] J. Muller, *J. Organometallic Chem.*, 1969, **18**, 321.

[5] P. E. Baikie, O. S. Mills, P. L. Pauson, G. H. Smith, and J. Valentine, *Chem. Comm.*, 1965, 425; P. E. Baikie, and O. S. Mills, *J. Chem. Soc.* (*A*), 1968, 2704.

his co-workers[6] detected an irreversible one-electron reduction process in [(π-C_7H_8)Mo$(CO)_3$].

Extending the delocalisation of the conjugated ring in *cycloheptatriene* species by replacing the methylene group by a keto-group as in [(π-tropone)Cr$(CO)_3$] caused an increase of the oxidation potential (relative to the C_7H_8 complex) of 280 mV.

The cationic cycloheptatrienyl complexes [(π-C_7H_7)Cr$(CO)_3$]$^+$ and [{π-C_7H_6(OMe)}Cr$(CO)_3$]$^+$ underwent irreversible, apparently one-electron, reduction processes, the nature of which will be discussed elsewhere;[7] no oxidation behaviour was detected. There is a substituent effect, the methoxy species having $E_{\frac{1}{2}}$ 490 mV more anodic than that of [(π-C_7H_7)Cr$(CO)_3$]$^+$.

EXPERIMENTAL

The voltammetric data were obtained using a Beckman Electroscan 30 polarograph under conditions described previously.[1] All complexes studied were obtained by standard procedures and their purity was established analytically, spectroscopically, and by m.p.

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[6] R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, 1966, **88**, 471.

[7] P. D. Frisch and J. A. McCleverty, to be published.