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SUBSTITUENT EFFECTS IN THE POLAROGRAPHIC REDUCTION OF t-BUTYL PHENYL KETONES AND METHYL BENZOATES COMPLEXED WITH $Cr(CO)_3$

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Summary

The effect of substituents in the aromatic ring on the half-wave potentials of the polarographic reduction of (t-butyl phenyl ketone)- and (methyl benzoate)-tricarbonylchromiums in dimethylformamide have been studied. The Hammett relationship is satisfactorily obeyed for both series of compounds, and the ρ values are practically equal to those measured for the analogous uncomplexed substrates. The results are interpreted in terms of a change in the electronic structure of the radical anion on passing from the free to the complexed ligand.

Introduction

Rates [1] and equilibria [2] of side-chain reactions of arene derivatives are strongly affected by the coordination of the ring with the $Cr(CO)_3$ group. It is usually accepted that the group behaves like a strong electron-withdrawing substituent although it can act as a source of electrons in reactions in which the α-carbon bears a substantial positive charge.

There is much interest in the question of whether the transmission of the electronic effects of the ring substituents through the arene skeleton is altered by the presence of the coordinated group. Thus, rate constants [1bef], equilibrium constants [2d] and proton chemical shifts [2c] have been plotted vs. Hammett σ's. All these reactions which involve a greater negative charge density in the final state than in the initial state are accelerated by the presence of the $Cr(CO)_3$ group and, more interestingly, the sensitivity to substituents of the complexed substrates, as expressed by ρ, is much lower than that for the corresponding free

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ligands. A significant case is the alkaline hydrolysis of substituted methyl benzoates, for which the ρ value drops from +2.36 to +1.55 following the complexation [1b].

In studying arenechromium tricarbonyl derivatives, our interest has recently turned to the elucidation of the effect of coordination on the electrochemical reduction in nonaqueous media. Electrochemical studies of tricarbonyl complexes in dipolar aprotic solvents are few, and in some cases controversial. Rieke [3] recently reported that arenechromium tricarbonyl hydrocarbons undergo electrochemical reduction by a simultaneous transfer of two electrons. The presence of a carbonyl in the hydrocarbon alters the nature of the process. For example, $(h^6\text{-}C_6H_5COCH_3)Cr(CO)_3$ undergoes a one electron reduction, though no direct evidence for a possible radical anion intermediate was obtained either by spectroscopic observation or by cyclic voltammetry, which indicated that the process is chemically irreversible. Almost at the same time we reported [4] that $(h^6\text{-}C_6H_5CO\text{-t-}C_4H_9)Cr(CO)_3$ is reduced by a reversible one electron process in dimethyl formamide. For this substrate both cyclic voltammograms and ESR observation of the ketyl radical confirmed the reversibility. Free t-butyl phenyl ketones are likewise reduced by a reversible one-electron process in dipolar aprotic media [5]. Thus, both the free and the coordinated t-butyl phenyl ketone appear to be reduced by the same mechanism. We have therefore undertaken the study of the effect of *meta* and *para* substituents on the half-wave potentials ($E_{1/2}$) in the polarographic reduction of complexed and uncomplexed t-butyl phenyl ketones. This provides informations on: (a) the mechanism of transmission of electronic effects in the complexed ring; (b) the electronic structure of the complexed ketyl radicals. We have also extended the polarographic study to the (methyl benzoate)tricarbonylchromiums.

Results

t-Butyl phenyl ketones. In anhydrous dimethyl formamide with tetra-n-butylammonium perchlorate as supporting electrolyte the free ketones (Table 1) display one defined wave. Logarithmic analysis and cyclic voltammetry at any scan rate used for each substrate showed that the reduction involves the reversible transfer of one electron which leads to the formation of the corresponding radical anion.

TABLE 1

HALF-WAVE POTENTIALS OF SUBSTITUTED t-BUTYL PHENYL KETONES, XC_6H_4CO-t-Bu, FREE AND COMPLEXED WITH $Cr(CO)_3$

X	σ	Free ketones ($-E_{1/2}$ ± 0.004) (V) [a]	Complexed ketones ($-E_{1/2}$ ± 0.004) (V) [a]
p-OMe	−0.27	1.884	1.392
m-t-Bu$_2$	−0.20 [b]	1.810	1.328
p-Me	−0.17	1.806	1.320
H	0	1.733	1.242
m-F	+0.34	1.572	1.084

[a] Potentials vs. Ag/AgBr electrode. [b] From ref. 17.

On the other hand, the complexed ketones (Table 1) display two distinct reduction waves, except for the *m*-fluoro compound which shows three waves. Both logarithmic analysis and cyclic voltammograms indicated that the first wave is still reversible *. The ESR observation of the complexed ketyl was obtained both electrochemically [4] and by chemical reduction. The splitting constants and the isotropic *g* factor have been given for the $[(h^6\text{-}C_6H_5CO\text{-}t\text{-}C_4H_9)Cr(CO)_3]^-$ K^+ ion pair in dimethoxyethane [6]. We conclude that the mechanism of the reduction which takes place at the first wave of the complexed ketones is similar to that for the free ketones. The second wave involves the reduction of the anion radical, as discussed elsewhere [4].

In Fig. 1.we show the plot of the $\Delta E_{1/2} = E_{1/2}(X) - E_{1/2}(H)$ vs. σ. The Hammett relationship is obeyed both by uncoordinated and coordinated ketones (correlation coefficients are 0.992 and 0.995, respectively). More interestingly, the slopes of the two lines have the same value (ρ = +0.48 V) within the experimental error. The two straight lines are separated by an interval of 0.5 V, the complexed ketones being reduced at less negative potentials.

Methyl benzoates. Base-catalyzed hydrolysis of methyl benzoates, both complexed and uncomplexed, is a bimolecular reaction of the S_N2(lim) type [1b]. Since the electrochemical reduction has been often compared to an S_N2 reaction with the cathode as nucleophile [7], it seemed interesting to see whether or not the heterogeneous process behaves like the homogeneous one.

We examined the reduction of eleven free substituted methyl benzoates (Table

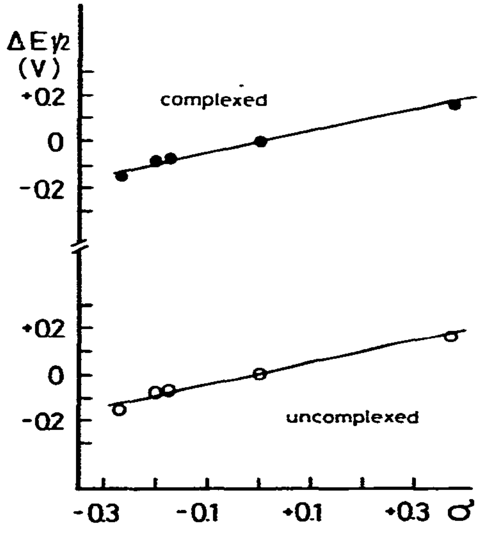

Fig. 1. Plot of $\Delta E_{1/2}$ of $XC_6H_4CO\text{-}t\text{-}Bu$, free and complexed with $Cr(CO)_3$, vs. Hammett σ. The open circles refer to the uncomplexed, the shaded circles to the complexed ketones.

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* We note that the variation of the intensity of the anodic peak relative to the cathodic peak at different sweep rates is evidence that the complexed radical anions decay more rapidly than the free ketyl radicals.

TABLE 2

HALF-WAVE POTENTIALS OF SUBSTITUTED METHYL BENZOATES, XC_6H_4COOMe, FREE AND COMPLEXED WITH $Cr(CO)_3$

X	σ	Free benzoates ($-E_{1/2} \pm 0.004$) (V) [a]	Complexed benzoates ($-E_{1/2} \pm 0.004$) (V) [a]
p-NH_2	−0.66	2.609	2.010
p-OH	−0.37	2.386	—
p-OMe	−0.27	2.400	1.802
p-Me	−0.17	2.290	1.721
m-Me	−0.07	2.247	—
p-F	−0.02 (σ^-)	2.238	1.648
H	0	2.221	1.640
p-Ph	+0.08 (σ^-) [b]	1.985	—
m-OMe	+0.11	2.183	1.624
m-F	+0.34	2.120	1.565
p-COOMe	+0.68 (σ^-)	1.631	1.303

[a] Potentials vs. SCE. [b] From ref. 18.

2) in dimethyl formamide with tetra-n-butylammonium perchlorate as supporting electrolyte. The reduction takes place in one well-defined diffusion wave for all substrates except the p-C_6H_5 and the p-$COOCH_3$ compounds, which display a second wave at more negative potentials. The logarithmic analysis of the curves, the potential sweep voltammetry, and the ESR observation for all substrates showed that the process consists in the reversible transfer of one electron.

$$ArCOOCH_3 + e^- \rightleftharpoons [ArCOOCH_3]^-$$

The reversibility of the electron transfer and the spectroscopic detection of the anion radicals agree with the results obtained by other authors [8].

The electrochemical study of the complexed methyl benzoates was carried out on eight substrates * (Table 2). The complexed esters show a single wave of reduction except the p-F benzoate which shows a second wave at more negative potentials, the nature of which was not further investigated. The reduction takes place at potentials much less negative than those of corresponding ligands (ca. 0.6 V) and probably again involves a one-electron transfer with formation of the complexed radical anions as the diffusion currents are of comparable height to those shown by equimolar solutions of (t-butyl phenyl ketone)- and (benzophenone)-tricarbonylchromium. Both substrates are reduced by a one electron process [4] and their diffusion coefficients are probably very similar to those of the esters examined. Also the value of 60 mV for the slope of the current-voltage curves strongly favours a one-electron reversible transfer. Unfortunately, we could not detect the radical anion intermediate. In contrast to the results for the free esters, in fact, the cyclic voltammograms at any sweep rate did not show any anodic peak associated with the cathodic peak and no ESR signal was detected on electrolysis of the p-H and p-$COOCH_3$ substrates in the cavity of the spectrometer. A possible explanation for the failure to detect the complexed

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* The complexation of p-C_6H_5 methyl benzoate gave only the isomer with the metal coordinated to the substituent phenyl group and the product could not be utilized to our purposes.

radical anions under conditions where the uncomplexed analogs are stable is that there is a rapid increase of the rate of the chemical processes which take place after the electron transfer. We ran a controlled potential electrolysis of the parent substrate which consumed about 1 F per mole. GLC analysis of the volatile products showed that CH_3OH was produced in 90% yield. TLC of non-volatile products, on the other hand, revealed the presence of two orange spots with R_f less than that of the complexed benzoate, indicating the formation of two different complexed compounds. These could be the products of condensation formed by nucleophilic attack of the radical anion on the depolarizer itself and/or the supporting electrolyte. In spite of the irreversible nature of the overall process, it seems reasonable to assume, on the basis of the polarographic data, that the reduction waves still refer to a fast one-electron transfer, which allows a comparison to be made between the $E_{1/2}$'s of the coordinated and uncoordinated esters.

The Hammett plots for the ligands and complexes are shown in Fig. 2. For the free ligands, nine out of eleven substituents are correlated by the relationship $\Delta E_{1/2}$ vs. σ. Least square analysis based on the nine substituents gave a value of $\rho = +0.49$ V (correlation coefficient $r = 0.975$). *p*-Phenyl and *p*-carbomethoxy groups, however, are definitely outside the regression line and their effect in shifting the $E_{1/2}$ to less negative values appears much stronger than that ascribable both to σ and σ^-. Conversely all the complexed esters are correlated by the Hammett relationship, included the *p*-carbomethoxy group. Least square analysis gave a value of $\rho = +0.49$ V (correlation coefficient $r = 0.985$).

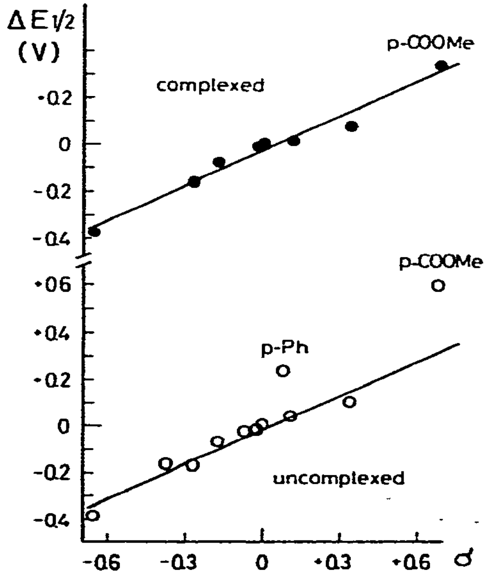
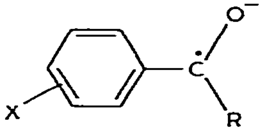


Fig. 2. Plot of $\Delta E_{1/2}$ of XC_6H_4COOMe, free and complexed with $Cr(CO)_3$, vs. Hammett σ. The open circles refer to the uncomplexed, the shaded circles to the complexed esters.

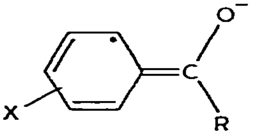
Discussion

The much greater electron affinity of the complexes in comparison with the free ligands, 0.5—0.6 V, has been interpreted in terms of lowering the energy of the lowest unoccupied molecular orbital and is a well documented phenomenon in the electrochemistry of arenechromium tricarbonyl derivatives [9]. The effect is analogous to that of the $Cr(CO)_3$ in increasing rates and equilibrium constants of those homogeneous reactions which involve a greater negative charge density in the final state than in the initial state and it is generally attributed to the strong electron-withdrawing capacity of the inorganic group. The controversial aspects of the matter have been recently discussed by Eaborn et al. [1f]. However, it is striking that in spite of the large shift of the $E_{1/2}$ to less negative values the complexing does not distort the pattern of the substituent effect. The Hammett relationship is satisfactorily obeyed both by the ketones and the esters and, most interestingly, the ρ values do not change at all with coordination. The complexes conform to the Hammett relationship in most of the homogeneous reactions which have been investigated, but comparable values of ρ for the complexed and uncomplexed substrates have not previously been observed, the complexes usually displaying values of ρ much lower than those of the corresponding ligands (the decrease is as much as 60% in the case of the pK_a's of phenols [2d]). The generally accepted explanation for this decrease of the influence of substituents by complexing consists in a simple saturation effect arising from the electron-withdrawing power of the $Cr(CO)_3$ group [1b,2cd] which should reduce the negative charge developed at the reaction center in the final state. Consequently the interactions between the substituent and the reaction center are diminished. A different explanation was proposed by Eaborn [1f] who suggested that the $Cr(CO)_3$ would act also as an electron reservoir by dampening the effect of both the electron-releasing and -withdrawing substituents.

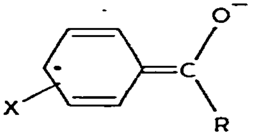
The finding that in the electrochemical reduction the sensitivity to substituents is not altered by the coordination does not agree with any of the above interpretations. Clearly, the main difference between the electrochemical and



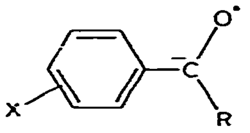
(Ia)



(Ib)



(Ic)



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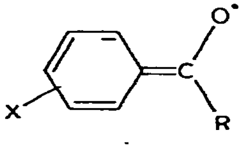

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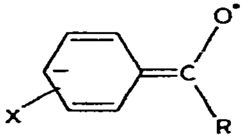

(IIc)

the chemical processes is the electronic nature of the final state, which in the reduction has an unpaired electron. Therefore, we believe that a reasonable interpretation of the substituent effects can be given only if we take into account the details of the electronic structure of the radical anions of the reduced ketones and esters. The radical anion of the free ligands can be represented by the limiting formulas Ia—Ic and IIa—IIc, where R = t-C_4H_9 in the ketones and R = OCH_3 in the esters.

If we first consider the free esters, a positive slope of 0.49 V cannot a priori distinguish which forms predominate in the resonance hybrid. The value of ρ reflects the sensitivity of the electrochemical process to the polar properties of the substituent which, to different extents influences both structures I and II. Some idea concerning the predominance of I or II comes from the interpretation of the anomalous behaviour of *p*-phenyl and *p*-carbomethoxy benzoates, which deviate quite largely from the regression line: *p*-phenyl deviates 0.2 V and *p*-carbomethoxy ca. 0.3 V. In other words, the two substituents manifest an extra-stabilization effect of the radical anion which is not accounted for either by their σ or σ^-. This effect can be explained in terms of a greater importance of the forms of I in the resonance hybrid. In these forms, the unpaired electron, not the charge, is delocalized over the aromatic substituted ring. The extraordinary ability of the biphenyl system in delocalizing the spin density [10] would account well for the strong shift of the $E_{1/2}$ from the regression line. The same applies to the *p*-carbomethoxymethyl benzoate, in which the substituent and the reduction center are indistinguishable and the unpaired electron is delocalized over the entire system [8a]. On this interpretation, the contribution to delocalize the spin density by the other substituents which are linearly correlated is not zero but must certainly be small, and about the same for all the members. The absolute value of ρ, therefore, represents mainly the ability of substituents to stabilize the negative charge in structures like I.

On the other hand, for the complexed esters all the substituents, including the *p*-$COOCH_3$, fit the Hammett relationship. The behaviour of the carbomethoxy group, as that of the other members, is well accounted for by its polar properties alone (failure to obtain the *p*-C_6H_5 derivative for study makes the subsequent discussion less certain than we would like). Consequently in contrast to the situation for uncoordinated species, where the ring is coordinated to $Cr(CO)_3$ forms analogous to II seem to make the more significant contribution to the resonance hybrid. Thus, the interaction between substituent and negative charge must be greater and this should be reflected in a greater ρ value than that for the uncomplexed substrates. This increased sensitivity to substituents arising from a different electronic structure of the complexed radical anion is countered by the "dampening" effect of the $Cr(CO)_3$ which still must operate. The net result is that the ρ values are equal in the complexed and uncomplexed esters, as though the inorganic group does not interfere at all with the transmission of the electronic effects. Our results are thus consistent with the view previously advanced on the basis of different evidence [11], that the metal carbonyl residue is a poor "sink" for the unpaired electron density which is localized mainly on the oxygen atom of the ligand, but it has a good capacity to delocalize negative charge on the ring and, eventually, on its own carbonyls.

The conclusions about the esters are certainly also valid for the ketones, for which the entire electrochemical process is reversible both for the complexed and the uncomplexed substrates. The similarity of the ρ values for the esters and the ketones is further evidence for the similarity of the process which is responsible of the electron transfer. Replacement of a OCH_3 group by a t-C_4H_9 should not much change the sensitivity to substituents.

Further support to our interpretation of the substituent effects on the basis of a different spin and charge distribution in the coordinated and uncoordinated anion radicals, comes from the ^{13}C splitting constants of the anion ketyl radicals obtained by chemical reduction. In this connection is it noteworthy that structures of type I for the metal ketyl radical of the benzophenone were suggested by Hirota [12] on the basis of the changes in the ^{13}C carbonyl splitting constants, which are very large in going from the free ketyl to the metal ketyl. We have run the ESR spectra of the ketyl radical of the complexed and uncomplexed t-butyl phenyl ketone in ethers containing alkali metals [13]. Unfortunately we could not measure the ^{13}C ketyl carbon splitting constant but we did obtain the ^{13}C splitting constant of the β carbons of the t-butyl group. There is a significant decrease of the ^{13}C splitting constant of the β carbons on going from the uncomplexed to the complexed compound. If a correlation exists between the ^{13}C β carbon and the ^{13}C ketyl carbon splitting constants, as suggested for comparable systems by Brière et al. [14], then on passing from the uncoordinated ketone to the coordinated one it appears that the spin density on the ketyl carbon is much diminished. This is in agreement with the suggestion that in the complexed ketyl radicals most of the spin is localized on the ketyl oxygen while the charge resides on the ketyl carbon, the aromatic ring and the $Cr(CO)_3$ group (forms analogous to II).

Experimental

Melting points are uncorrected. Microanalyses were performed by Mr. L. Turiaco, Istituto di Chimica Analitica, Padova, Italy.

Commercial grade DMF was purified by distillation at reduced pressure after drying for several days over K_2CO_3. Tetra-n-butylammonium perchlorate, made from tetrabutylammonium hydroxide and perchloric acid, was crystallized twice from ethanol and dried in vacuo at 50°C. Commercial grade di-n-butyl ether was dried over Na/K alloy and distilled just before the use.

t-Butyl phenyl ketones

Free ketones. t-Butyl phenyl ketone [15] and t-butyl *p*-methoxyphenyl ketone [16] were prepared by published methods. The *p*-CH_3, *m*-F and *m*-$(t\text{-}C_4H_9)_2$ substituted ketones were prepared by the method of Pearson [15] from t-butyl cyanide and the appropriate bromobenzene. Physical properties, IR and NMR spectra were as expected. The new compound *m*-$(t\text{-}C_4H_9)_2$ had m.p. 32°C and b.p. 118—122°C/0.5 mmHg (Found: C, 82.8; H, 11.5. $C_{19}H_{30}O$ calcd.: C, 83.1; H, 11.1%). IR (neat): $\nu(C{=}O)$ 1675 cm^{-1}.

Complexed ketones. The complexes were prepared by refluxing under nitrogen ca. 2 *M* oxygen-free solutions of the ketones in anhydrous di-n-butyl ether with a twice molar ratio of $Cr(CO)_6$. After removal of the solvent and of the unreacted ligand at reduced pressure, the crude products were crystallized from

TABLE 3

PROPERTIES OF (h^6-XC_6H_4CO-t-Bu)$Cr(CO)_3$ COMPLEXES

X	Colour	M.p. (°C)	Analysis found (cald.) (%)	
			C	H
H	Orange	64	56.6 (56.7)	4.65 (4.69)
p-Me	Orange	97	57.3 (57.8)	4.82 (5.16)
p-OMe	Yellow	81	55.2 (54.9)	4.99 (4.91)
m-t-Bu_2	Orange	96	64.5 (64.6)	7.56 (7.48)
m-F	Red	60	52.7 (53.2)	3.89 (4.14)

ethyl ether/hexane. Physical properties are listed in Table 3. The IR and NMR spectra were consistent with the indicated structures.

Methyl benzoates

Free benzoates. The esters were prepared by refluxing the appropriate benzoic acid in methanol in the presence of sulphuric acid. NMR spectra and physical properties were as expected.

Complexed benzoates. The coordinated esters were prepared from the corresponding benzoates and $Cr(CO)_6$ as described by Klopman and Calderazzo [1b], and characterized by their melting points and elemental analyses. Physical characteristics of three new compounds are reported in Table 4. IR and NMR spectra were consistent with their structure.

Apparatus

IR spectra were run on a Beckman IR-9 grating infrared spectrophotometer. NMR spectra were recorded on a Bruker HFX-90 MHz spectrometer as 5% $CDCl_3$ solutions (internal TMS). ESR spectra were recorded at room temperature on a Varian E-3 spectrometer operating with a 100 KHz field modulation.

TABLE 4

PROPERTIES OF (h^6-XC_6H_4COOMe)$Cr(CO)_3$ COMPLEXES

X	Colour	M.p. (°C)	Analysis found (calcd.) (%)	
			C	H
p-F	Orange	103—105	45.8 (45.5)	2.49 (2.43)
m-F	Orange	82—84	45.9 (45.5)	2.31 (2.43)
m-OMe	Orange	57—59	47.3 (47.6)	3.33 (3.33)

Polarographic and voltammetric experiments were carried out with an Amel 448 oscillographic polarograph. The counter electrode was a mercury pool. An Ag/AgBr, Br^- 0.1 M in CH_3CN electrode was used as reference for ketones; a SCE electrode was employed for esters.

Controlled-potential coulometric experiments were performed with an Amel model 557 potentiostat equipped with an Amel 558 integrator; the working electrode was a mercury pool.

Gas chromatographic experiments were carried out with a Varian 1200 Aerograph apparatus equipped with a K 20 M Carbowax column.

Acknowledgements

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