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THE RELATIVE BASE STRENGTHS OF THE $Cr(CO)_3$, $Mo(CO)_3$, AND $W(CO)_3$ COMPLEXES OF TROPONE

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Summary

π-Complexation of tropone with $Cr(CO)_3$, $Mo(CO)_3$, and $W(CO)_3$ groups increases the ketonic base strength in water by ca. 2 pK units, with only a small metal dependence in the sequence Mo ≈ W > Cr.

Introduction

There are puzzling features and inconsistencies in the reported metal dependence of the chemical reactivity of organic ligands in complexes with the transition metals of a particular triad, e.g. $EtOC(R){=}M(CO)_5$ [1], $[(\eta^7\text{-tropylium})M(CO)_3]^+$ [2] (M = Cr, Mo, and W) and $[(\eta^5\text{-cyclohexadienyl})M(CO)_3]^+$ [3], $[(\eta^5\text{-pentafulvene})MCp]^+$ [4], $[(\eta^6\text{-benzene})_2M]^{2+}$ [5] (M = Fe, Ru, and Os), and no clear pattern has emerged from the available data.

We recently reported that π-complexation of tropone and its 2-alkoxy derivatives with a $Cr(CO)_3$ group causes a substantial increase in the ketonic base strength, as indicated by the pK_a values for the corresponding conjugate acids in water [6]. As an extension of this work, we have determined the pK_a values for the corresponding $Mo(CO)_3$ and $W(CO)_3$ complexes, in order to assess the metal dependence of this base-enhancement effect.

Results and discussion

The tropone complexes Ib, Ic were synthesised by the reactions of tropone with $(MeCN)_3M(CO)_3$ (M = Mo and W). These complexes are much less stable towards decomposition than is the Cr analogue Ia, and it was found convenient to isolate and purify the BF_4^- salts of the conjugate acids IIb, IIc, which were obtained by treatment of the crude reaction products with HBF_4. These salts are relatively stable in strong aqueous acids and in non-basic anhydrous solvents. Dissolution of the salts (IIa–IIc)(BF_4^-) in basic solvents such as pyridine, or in water, causes quantitative deprotonation to give the tropone complexes Ia–Ic. However, whereas the Cr

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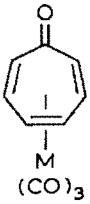
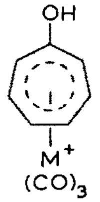
complex Ia is stable in solution for prolonged periods, the Mo (particularly) and W analogues decompose with liberation of the tropone ligand; in water of pH ca. 6 at 25°C, the half-lives of Ib and Ic are ca. 9 and 60 minutes, respectively.

The pK_a values for IIb and IIc were determined for aqueous $HClO_4$ solutions using the method previously described [6] for the Cr complex (IIa), but ensuring that each determination was completed before decomposition of the substrate had become significant. The results (Table 1) show that each of the metal-complexed tropones is much more basic (by ca. 2 pK units) than is tropone (p$K_a = -0.82$ [6]) itself, with a relatively small metal dependence Mo ≈ W > Cr. The difference between the pK_a values for the Mo and W systems is within experimental uncertainty, these complexes (Ib,Ic) being more basic than the Cr complex Ia by ca. 0.25 pK unit.



(I)



(II)

(a, M = Cr; b, M = Mo; c, M = W)

We pointed out previously that the enhanced basicity of the Cr-complexed tropones, relative to that of tropone, is a consequence of the greater stabilisation that metal complexation confers on the conjugate acid IIa than on the tropone complex Ia [6]. The present results suggest that complexation of a hydroxytropylium cation with an $Mo(CO)_3$ or $W(CO)_3$ group results in slightly greater stabilisation of the system than that provided by a $Cr(CO)_3$ group. Earlier work [2a] leading to the conclusion that the thermodynamic stabilities of $[(\eta^7\text{-tropylium})M(CO)_3]^+$ (M = Cr, Mo, and W) in solution are independent of the identity of the metal has been shown [7] to have been misinterpreted, and the relative electrophilic reactivities of these cations appear to vary from reaction to reaction [2b–2d]. Further kinetic and thermodynamic measurements are required before stability-reactivity-selectivity relationships for such series of organometallic systems can be properly assessed.

TABLE 1

pK_a DETERMINATIONS [a]

System	Absorption max. (nm)		Analytical wavelength (nm)	pK_a
	(I)	(II)		
(IIa) ⇄ (Ia)	326	318	335	1.14 ± 0.08 [b]
(IIb) ⇄ (Ib)	318	306	326	1.40 ± 0.04
(IIc) ⇄ (Ic)	313	299	320	1.34 ± 0.04

[a] For aqueous solutions at 25.0°C. Values given are the mean of several independent determinations.
[b] Reported previously [6].

Experimental

For general remarks, see ref. 6. Hexacarbonyl-molybdenum and -tungsten (Strem Chemicals) were used as supplied.

Preparation of salts (IIb,IIc) (BF_4^-)

A mixture of tropone (0.6 g; 5.7 mmol) and $(MeCN)_3M(CO)_3$ (7.5 mmol), prepared [9] from $Mo(CO)_6$ or $W(CO)_6$, in anhydrous THF (25 ml) was heated under reflux for 0.5 h in an atmosphere of dry N_2. The solvent was then evaporated under reduced pressure and a solution of 40% aqueous HBF_4 (1 g) in acetone (10 ml) was added to the residue. The mixture was stirred for 5 min, then filtered, and the filtrate was evaporated to dryness under reduced pressure. The pure product was obtained by repeated recrystallisation of the residue from acetone/ether.

The salt (IIb)(BF_4^-) was obtained in 52% yield as a yellow powder, m.p. 286–288°C (decomp.); IR (KBr), 2055, 2000, 1990 cm^{-1}; ^1H NMR (CF_3CO_2H), δ 5.7–6.5 (m) ppm.

The salt (IIc)(BF_4^-) was obtained in 15% yield as an orange-yellow powder, m.p. 232–234°C (decomp.); IR (KBr), 2050, 1970 cm^{-1}; ^1H NMR (CF_3CO_2H), δ 5.6–6.4 (m) ppm.

These salts decompose slowly on storage and elemental analyses were not obtained. For comparison, the known salt (IIa)(BF_4^-) [6,8] has m.p. 180–181°C (decomp.); IR (KBr), 2040, 1995 cm^{-1}; ^1H NMR (CF_3CO_2H), δ 5.9–6.9 (m) ppm.

Attempted isolation of tropone complexes (Ib,Ic)

Attempts to isolate and purify the tropone complexes (Ib,Ic), formed in the ligand-exchange reactions, were unsuccessful because of their instability in solution towards decomposition to tropone and grey-brown metal-containing species. In water of pH ca. 6 at 25°C, the rates of decomposition of Ib and Ic at a concentration of ca. 10^{-4} *M* are first-order in [substrate]. The Cr complex Ia, on the other hand, is stable both as a solid and in solution [6,8]. Dissolution of the salts (IIa–IIc)(BF_4^-) in pyridine-d_5 gave solutions of the corresponding tropone complexes whose ^1H NMR spectra were recorded: Ia, δ 6.6–7.1 (m); Ib, 6.5–7.1 (m); Ic, 6.6–7.1 (m) ppm.

pK_a determinations

The method detailed [6] previously for the Cr complex was used. Following successive additions of 5 μl aliquots of aqueous $HClO_4$ (11.70 *M*) to a solution (2.5 ml) of tropone complex (1.5×10^{-4} *M*) in water (obtained by dissolution of freshly purified conjugate acid salt) at 25.0°C, the relative equilibrium concentrations of ketone (I) and protonated ketone (II) were calculated from the absorbance at a suitable wavelength. These wavelengths and those of maximum absorbance of the substrates are in Table 1. Upon each addition of acid, equilibrium between I and II was established instantaneously, and all of the measurements were completed before decomposition of the tropone complex had become significant (cf. rates of decomposition were determined separately). The conjugate acids IIb, IIc are relatively stable towards decomposition in aqueous acid. For each determination, solutions (at least five) giving 20–75% protonation of the tropone complex were used. Each determination was repeated several times (at least four) and reproducible results were found.

For the equilibrium:

$$\mathrm{II} + H_2O \overset{K_a}{\rightleftarrows} \mathrm{I} + H_3O^+$$

the following relationships apply:

$$[H_3O^+] = K_a\{[\mathrm{II}]/[\mathrm{I}]\} \tag{1}$$

$$-\log[H_3O^+] = \log\{[\mathrm{I}]/[\mathrm{II}]\} + pK_a \tag{2}$$

Plots of $[H_3O^+]$ against the equilibrium ratio [II]/[I] for the sets of data from each determination were linear (correlation coefficients $\geqslant 0.997$), and K_a was taken as the slope of the least-squares best-fit line. The corresponding pK_a values are in Table 1. Plots of $-\log[H_3O^+]$ against $\log\{[\mathrm{I}]/[\mathrm{II}]\}$ were also linear with slopes near unity in accord with eq. 2.

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