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THE EFFECT ON THE BASE STRENGTHS OF TROPONE AND 2-ALKOXYTROPONES OF π-COMPLEXATION WITH A $Cr(CO)_3$ GROUP

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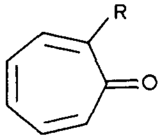
Summary

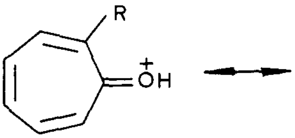
π-Complexation of tropone and its 2-methoxy and 2-ethoxy derivatives with a $Cr(CO)_3$ group causes an increase in the ketonic base strength by 1.7 ± 0.3 pK units.

Introduction

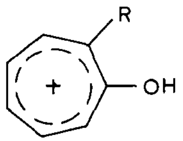
Tropone (**1a**) and its ring-substituted derivatives are much more basic than most other unsaturated ketones because their conjugate acids have aromatic stabilisation as hydroxytropylium cations (**2A** ↔ **2B**) [1]. We have recently shown [2,3] that π-complexation of tropylium cation (Tr^+) with a $Cr(CO)_3$ group causes a substantial increase in thermodynamic stability; for example, the pK_{R^+}-values for Tr^+ and $[(\eta\text{-}Tr)Cr(CO)_3]^+$ in methanol are 2.15 [4] and 6.5 [3], respectively. It appeared



(1)



(2A)



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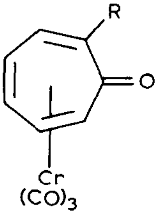

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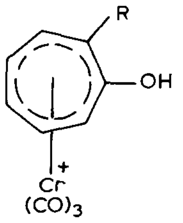

(4)

a; R = H
b; R = OH
c; R = OMe
d; R = OEt

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possible, therefore, that π-complexation of tropone and its derivatives with $Cr(CO)_3$ would lead to an enhancement of the ketonic base strength. In this paper, we show that this is indeed the case.

Results and discussion

The tropone complex **3a** was synthesised according to the literature method [5] by the ligand-replacement reaction of $(MeCN)_3Cr(CO)_3$ with tropone (**1a**). Attempts to prepare the related complex **3b** from tropolone (**1b**) by the same method were unsuccessful. This reaction instead afforded a dark red product, possibly a chelated tropolonate-chromium complex, which was not characterised. However, reactions of $(MeCN)_3Cr(CO)_3$ with the 2-alkoxytropones (**1c**,**1d**), which were prepared by base-promoted alkylations of tropolone, afforded low yields of the corresponding π-complexes (**3c**,**3d**). The BF_4^- salt of the hydroxytropylium complex (**4a**) was readily obtained [5] by the reaction of **3a** with HBF_4.

The pK_a value for the conjugate acid of tropone itself has been measured by two groups who obtained values of −0.6 [6] and −1.02 [1b]. In view of the discrepancy, we repeated the determination for solutions in strong aqueous H_2SO_4 and obtained a value of −0.82, based on the Deno H_0 acidity function. The pK_a values for the conjugate acids of 2-methoxy- and 2-ethoxy-tropone were measured similarly and values of −0.40 and −0.35, respectively, were found. Thus, the basicity of tropone is modestly enhanced by a 2-alkoxy substituent. These tropones (**1**) are therefore ca. 6 p*K* units more basic than most other organic carbonyl compounds whose conjugate acids have pK_a values in the range −6 to −7 [7].

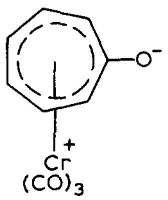
The metal complexes **3a**,**3c**,**3d** were found to be much more basic than the uncomplexed tropones such that the pK_a values for their conjugate acids (**4a**,**4c**,**4d**) could be determined using aqueous HCl or $HClO_4$ solutions. Independent experiments established that reactions of the 2-alkoxytropone complexes (**3c**,**3d**) with protic acids, under the conditions of the pK_a determinations, do not cause dealkylation but involve only reversible protonation of the ketonic group. Comparison of the pK_a values (Table 1) for the metal-free and metal-complexed systems shows that the base strength of tropone is increased by ca. 2 p*K* units as a result of π-complexation with a $Cr(CO)_3$ group; i.e., the organometallic cation (**4a**) is a weaker acid than the conjugate acid of tropone (**2a**). The base strengths of the 2-alkoxytropones are

TABLE 1

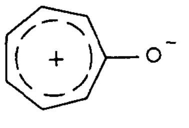
pK_a DETERMINATIONS [a]

System	Absorption max. (nm)		Analytical wavelength (nm)	pK_a
	Protonated tropone	Tropone		
2a ⇄ **1a**	311	312	326	−0.82 ± 0.02
2c ⇄ **1c**	302,341	316,346	361	−0.40 ± 0.01
2d ⇄ **1d**	302,344	316,347	361	−0.35 ± 0.01
4a ⇄ **3a**	270,318	326	335	1.14 ± 0.08
4c ⇄ **3c**	248,325	254,332	336	1.06 ± 0.02
4d ⇄ **3d**	265,339	270,348	354	1.13 ± 0.02

[a] For aqueous solutions at 25.0°C.



(5)



(6)

likewise enhanced by metal complexation, but to a somewhat smaller degree (by ca. 1.5 pK units). However, the pK_a values show that the base strength of the tropone complex **3a** is not significantly affected by the introduction of a 2-alkoxy substituent, in contrast to the response in the metal-free system (see above).

The crystal structure [8] of the tropone complex **3a** shows that there is no significant bonding between the metal atom and the ketonic carbon atom, and that the ketonic bond length (1.23 Å) is typical of an organic carbonyl group. These and other structural features are consistent with (η^6-triene)metal bonding but not with a dipolar (η^7-tropylium)metal formulation (**5**). On the other hand, calculations [1a] suggest that the dipolar oxytropylium structure (**6**) makes an appreciable contribution (ca. 16%) to the ground-state character of tropone. It appears, therefore, that π-complexation of tropone with a $Cr(CO)_3$ group may cause a reduction in the extent of polarisation of the ketonic carbonyl group. Comparison of the spectroscopic properties (Experimental) of the conjugate acid of the tropone complex with those for $[(\eta\text{-Tr})Cr(CO)_3]^+$ [2] and the tropone complex **3a** itself suggests that there is appreciable (tropylium)metal character in the structure of the conjugate acid, as shown **4a**. Likewise, the properties of the conjugate acid of tropone itself indicate a hydroxytropylium structure (**2Ba**) [1a]. The enhanced basicities of tropone complexes of the type (**3**), as revealed by the pK_a values (Table 1), is thus a consequence of the greater stabilisation that metal π-complexation confers on the protonated tropones than on the tropones themselves.

Experimental

All reactions involving organometallic substrates were conducted under an atmosphere of dry, oxygen-free N_2. Solvents were thoroughly dried and redistilled before use. Petrol refers to the fraction of b.p. 40–60°C. M.p.'s are uncorrected. Tropone (Lancaster Synthesis), tropolone (Aldrich Chemical Co.), and hexacarbonylchromium (Strem Chemicals) were used as supplied. The complexes **3a**- and **4a**-(BF_4^-) were synthesised by the reported methods [5]. Electronic, ^1H NMR, and IR spectra were obtained using, respectively, a Unicam SP1700 spectrometer, a Perkin–Elmer R32 (90 MHz) spectrometer, and a Perkin–Elmer 457 spectrometer.

2-Methoxytropone (1c). A mixture of tropolone (0.20 g; 1.6 mmol), iodomethane (0.50 g; 3.5 mmol), and potassium carbonate (0.40 g; 2.9 mmol) in anhydrous acetone (20 ml) was heated under reflux with stirring for 3 h. The mixture was then cooled and filtered, and the residue was washed with anhydrous acetone (5 ml). The filtrate was evaporated under reduced pressure, leaving an oil which crystallised from CCl_4 giving pure product **1c** (0.19 g, 85%), m.p. 35–36°C (lit. [9], 37–38°C).

*2-Ethoxytropone (**1d**).* A mixture of tropolone (2.8 g; 23 mmol), bromoethane (10 g; 92 mmol), and potassium carbonate (3.5 g; 25 mmol) in anhydrous dimethyl sulphoxide (25 ml) was stirred at room temperature for 16 h. The mixture was then poured into brine made slightly acidic with HCl, and the solution was extracted with $CHCl_3$ (4 × 50 ml). The organic extract was washed with brine until neutral, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed on silica gel. Ether/methanol (95/5 v/v) eluted the product **1d** (2.4 g; 70%), a liquid with properties identical to those reported [10].

*2-Alkoxytropone complexes (**3c,3d**).* The following general method was used. A mixture of the 2-alkoxytropone (7.4 mmol) and $(MeCN)_3Cr(CO)_3$, prepared [11] from $Cr(CO)_6$ (2.0 g; 9.1 mmol), in anhydrous THF (25 ml) was heated under reflux for 0.5 h. The mixture was then evaporated to dryness under reduced pressure, and the residue was extracted with boiling ether or petrol. Evaporation of the extract gave pure product.

Tricarbonyl(η-2-methoxytropone)chromium (**3c**) was obtained (0.40 g, 20%) as an orange solid, m.p. 100–101°C (decomp.); IR (KBr): 1992, 1920, 1904 (ligand CO), and 1605 cm^{-1} (ketonic CO); ^1H NMR ($CDCl_3$), δ 3.78 (s, OMe) and 4.9–6.0 ppm (m, vinyl protons).

Tricarbonyl(η-2-ethoxytropone)chromium (**3d**) was obtained (0.46 g, 24%) as a viscous orange liquid; IR (film), 1995, 1935 (ligand CO), and 1600 cm^{-1} (ketonic CO); ^1H NMR ($CDCl_3$), δ 1.46 (t, Me), 4.10 (q, CH_2), and 4.9–6.0 ppm (m, vinyl protons).

Attempted preparation of tropolone complex (3b)

The reaction between tropolone and $(MeCN)_3Cr(CO)_3$ in THF was carried out as in the preceding experiment. There was obtained a dark red crystalline product, m.p. > 230°C, insoluble in petrol and ether but soluble in $CHCl_3$; IR (KBr), 2010, 1960, 1940, and 1540 cm^{-1}; no ^1H NMR signals were observed for solutions in $CDCl_3$, suggesting a paramagnetic species. This product, which was clearly not the desired complex **3b**, was not investigated further.

pK_a determinations

The following method was used for the tropones **1a,1c,1d**. A series of aqueous H_2SO_4 solutions of accurately known concentrations spanning the range 5–50% w/w was prepared. To each solution (exactly 2.5 ml) in a 1 cm cuvette, thermostatted at 25.0°C, an exact volume (typically 50 μl) of a stock solution of the tropone (10^{-2} *M*) in water was added and the UV spectrum of the resulting solution was recorded (200–400 nm). Each tropone was almost completely protonated (> 97%) in 50% w/w aqueous H_2SO_4, giving the spectrum of the corresponding conjugate acid; the spectrum of the tropone itself was obtained in water. Wavelengths of absorption maxima for the two species are in the Table 1. By comparison of these spectra, a suitable wavelength of maximum absorbance change was selected for analysis (Table 1). The relative equilibrium proportions of the tropone and its conjugate acid in the aqueous H_2SO_4 solutions were calculated from the absorbances at this wavelength. For determination of the pK_a value, solutions (at least 10) giving 15–80% protonation of the tropone were used. The sets of spectra for each system showed good agreement with the Lambert–Beer law, with at least one isobestic point. The determinations were repeated several times and reproducible results were obtained.

$$[H^+] = K_a\{[BH^+]/[B]\} \tag{1}$$

$$-\log[H^+] = \log\{[B]/[BH^+]\} + pK_a \tag{2}$$

The relationships 1 and 2 apply where [B] and $[BH^+]$ are the relative equilibrium concentrations of the tropone and its conjugate acid, respectively, in a solution of effective acid concentration $[H^+]$. For the strong aqueous H_2SO_4 solutions required, $-\log[H^+]$ was equated to the Deno H_0 acidity function; numerical values of H_0 for the various acid concentrations were obtained from literature values [12] by interpolation. For each system, plots of H_0 against $\log\{[B]/[BH^+]\}$ were linear (correlation coefficients ≥ 0.995) with slopes in the range 0.93 ± 0.06. From equation 2, the pK_a value (Table 1) was taken from the least-squares best-fit line as the H_0 value for a solution in which $[B] = [BH^+]$.

A modified procedure was used for the metal-complexed tropones **3a**,**3c**,**3d**. Aliquots (exactly 5 μl) of aqueous HCl (10.0 M) were added successively to a solution (exactly 2.5 ml) of the complex (1.5×10^{-4} M) in water at 25.0°C and the UV spectra of the resulting solutions were recorded after each addition. The spectrum of the tropone complex was obtained in water and of its conjugate acid in aqueous acid of sufficient strength to ensure > 97% protonation. For each solution, the relative equilibrium concentrations of the protonated and unprotonated tropone complexes (i.e., $[BH^+]/[B]$) were calculated from the absorbance at a suitable wavelength (Table 1), making appropriate corrections for the dilution factor. Repeated determinations gave reproducible results. The entire procedure was then repeated using aqueous $HClO_4$ (12.0 M) in place of HCl. The sets of spectra for each system showed two isosbestic points. Plots of $[H^+]$ against $[BH^+]/[B]$ for each set of data were linear (correlation coefficients ≥ 0.994) and, from equation 1 the K_a values were obtained from the slopes of the least-squares best-fit lines. Good agreement was found between the values calculated from data for independent determinations using both HCl and $HClO_4$. The corresponding pK_a values are in Table 1. Plots of $-\log[H^+]$ against $\log\{[B]/[BH^+]\}$ were also linear with slopes near unity, in accord with equation 2.

Reversibility of protonation of complexes

Each of the complexes **3a**,**3c**,**3d** was dissolved in aqueous solutions of sufficient acid strength to ensure complete protonation. These solutions were then diluted with water and extracted with ether. The starting complexes were recovered in good yields. Dissolution of the salt **4a** (BF_4^-) in water gave the tropone complex **3a** quantitatively.

Spectroscopic properties

$[(\eta\text{-Tr})Cr(CO)_3]^+$: UV (MeCN, BF_4^- salt), $\lambda_{max.}$ 270 ($\log \epsilon = 4.01$), 290 nm (shoulder, $\log \epsilon = 3.82$); ^{1}H NMR (CF_3CO_2H), δ 6.6 ppm (s).

3a: UV (MeCN), λ_{max} 330 nm ($\log \epsilon = 3.95$); ^{1}H NMR ($CDCl_3$), δ 4.8–5.3 (m, 2H), 5.5–6.0 ppm (m, 4H).

4a: UV (MeCN, BF_4^- salt), λ_{max} 270 ($\log \epsilon = 3.94$), 316 nm ($\log \epsilon = 3.96$); ^{1}H NMR (CF_3CO_2H), δ 6.0–7.0 ppm (m).

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