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Preliminary communication

A COMPARISON OF THE STABILITY AND REACTIVITY IN SOLUTION OF THE TROPYLIUM CATION AND ITS π-$Cr(CO)_3$ COMPLEX

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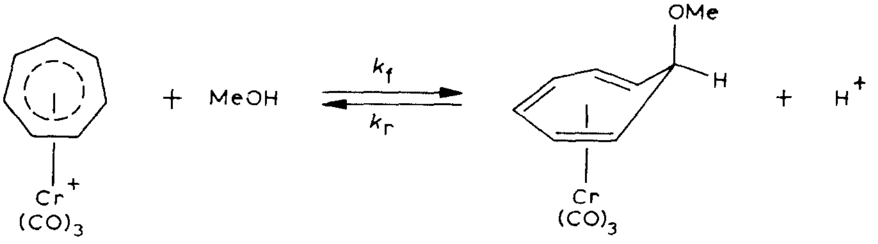
Summary

π-Complexation of the tropylium cation with a $Cr(CO)_3$ group greatly reduces its reactivity towards addition of methanol and enhances to a smaller degree its rate of formation by acid heterolysis of tricarbonyl(η-7-*exo*-methoxycycloheptatriene)chromium (2); the metal-complexed carbocation 1 is stable in aqueous solutions of pH $\leqslant$ 7, but at higher pH neutral products form irreversibly. Conversion of 2 into 1 in $MeCN/H_2O$ (1/1 w/w) is general acid-catalysed.

The stabilities and reactivities of neutral π-hydrocarbons are often sensitive to attachment of a transition metal-ligand group. The effects of metal complexation on the properties of π-carbocations are less well documented because few uncomplexed carbocations are sufficiently stable in solution to allow kinetic study of their reactions. Thermodynamic stabilities of benzyl and diphenylmethyl cations are increased by complexation of the phenyl rings with $Cr(CO)_3$ (cf. pK_{R^+} values [1]) but these organic cations are too reactive towards nucleophiles to allow direct comparison of rates of addition with those for the corresponding organometallic systems. Early work suggested that the stability in water of the tropylium cation (Tr^+) relative to that of tropyl alcohol (TrOH) is increased by π-complexation with $M(CO)_3$ (M = Cr, Mo, and W) [2] and that the degree of stabilisation and the rates of nucleophilic additions [3] to these metal-complexed carbocations are relatively insensitive to the identity of the metal, but there has been no thorough kinetic study of these systems.

We have studied addition of MeOH to the BF_4^- salt of the cation 1 and the reverse reaction, i.e., acid heterolysis of the 7-*exo*-methoxycycloheptatriene complex (2) in MeOH (eq. 1). Rates of the corresponding reactions of Tr^+ and

TrOMe in MeOH have been reported [4]. Preliminary results show that 1 is ca. 2×10^3 times less reactive than Tr^+ towards addition of MeOH (the solvent), with a first-order rate constant (k_f) of 0.07 s^{-1} at 25.0 °C, and that 2 is ca. 20 times more reactive than TrOMe towards acid heterolysis in MeOH, based on $k_r = 2.2 \times 10^5$ l mol^{-1} s^{-1} in MeOH at 25.0 °C with 0.5—2.0 m*M* $HClO_4$, so that pK_{R^+} is ca. 6.5. This value is ca. 4.3 p*K* units more positive than that for Tr^+ in the same solvent [4]. Added salts (e.g. $NaClO_4$, NaOTs, CF_3CO_2Na) retard addition of MeOH to 1, as found for nucleophilic additions to other carbocations [5]. The 7-*endo*-methoxy isomer of 2 is very much less reactive towards acid heterolysis than is 2 [6].



(1) (2) (1)

Conversion of 2 into 1 can also be followed in H_2O/MeCN (1/1 w/w) with 0.5—6.0 m*M* $HClO_4$ and $k_r = 3.4 \times 10^4$ l mol^{-1} s^{-1} at 25.0 °C. Reaction is general acid-catalysed and the second-order rate constants (k_r^{HA}) are 1.2×10^2 and 1.6×10^3 l mol^{-1} s^{-1} for cyanoacetic and dichloroacetic acid buffers, respectively, corresponding to a Brønsted α-value in the range 0.8—0.9 (based on pK_a values in aqueous MeCN [7]). The 7-*endo*-methoxy isomer of 2 is not converted into 1 in aqueous acid solutions (up to 2 *M* HCl or $HClO_4$) but instead undergoes slow decomplexation giving Tr^+ finally [6].

The cation 1 is stable, and does not add H_2O, in aqueous solutions of pH $\leqslant$ ca. 7. At higher pH in aqueous solvents, irreversible loss of 1 gives a mixture of the mono- and bis-[$Cr(CO)_3$] complexes of ditropyl [8]; tropyl alcohol is also formed but there is no evidence for the presence of the $Cr(CO)_3$ complex of this alcohol. We are studying the mechanism of this reaction; it seems likely that, in alkaline solutions, breakdown of the complex affords a Cr species which can effect one-electron reduction of 1 leading to dimerisation. Interestingly, [(η-methoxytropylium)$Cr(CO)_3$]$^+$ [9] is cleanly and quantitatively converted into [(η-tropone)$Cr(CO)_3$] in aqueous solutions of pH $\geqslant$ ca. 8 [6].

A change of solvent from MeOH to H_2O generally increases pK_{R^+}; e.g., values for Tr^+ in MeOH and H_2O are 2.15 and 4.7, respectively [4]. Thus, our estimate of pK_{R^+} = ca. 6.5 for 1 in MeOH is inconsistent with the reported value of 6.3 [2] in H_2O. Addition of 2 to aqueous $NaHCO_3$ buffers of pH 7.8—8.4 gives fairly rapid and quantitative formation of 1 which is then converted into the neutral products described earlier. Consequently, pK_{R^+} for 1 must be > 9, if it is at all meaningful to cite a value for a system that does not exhibit reversible carbocation $\rightleftarrows$ alcohol behaviour. The earlier determination [2] of pK_{R^+} for 1 in H_2O was apparently misinterpreted, and the effect on carbocation stability of changing the metal through the series $[(\eta\text{-Tr})M(CO)_3]^+$ (M = Cr, Mo, and W) must be regarded as an open question.

Finally, given our value of 0.07 s^{-1} for the first-order rate constant (k^{MeOH}) for addition of MeOH to 1 and the earlier finding [4] that the relative rate constants (k^{MeO^-}/k^{MeOH}) for additions of MeO^- and MeOH to Tr^+ and substituted tropylium cations are all $> 2 \times 10^6$, the first-order rate constant (k 13 s^{-1}) reported [3] for addition of MeO^- (0.125 *M*) to 1 in H_2O (!) is anomalously low, The conclusion from this study [3] that the cations $[(\eta\text{-Tr})M(CO)_3]^+$ (M = Cr, Mo, and W) have similar reactivities towards MeO^- merits reinvestigation. In this connection, we have recently found [10] that the relative rates of transfer of MeO^- from (MG)OMe (MG = Malachite Green) to Tr^+, $[(\eta\text{-Tr})Cr(CO)_3]^+$, $[(\eta\text{-Tr})Mo(CO)_3]^+$, and $[(\eta\text{-Tr})W(CO)_3]^+$ are 110/1/10/6, respectively.

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