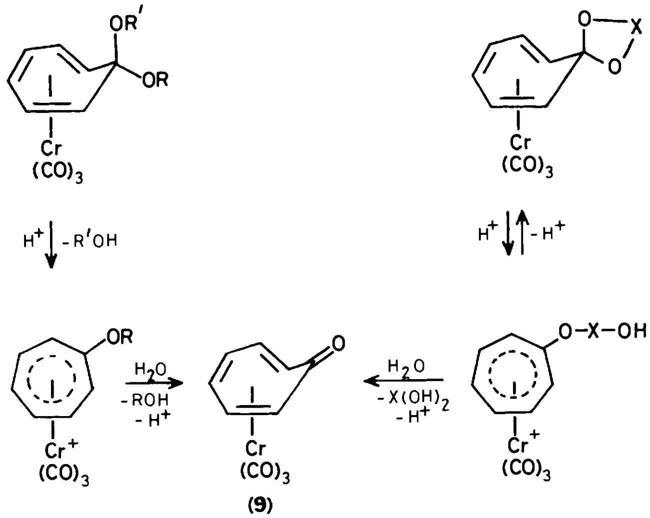
Kinetic Study of the Effect of $(OC)_3Cr$ π-Complexation upon the Reactivities of Tropone Acetals and Related Tropylium Cations

Nigel T. Leckey and William E. Watts *
Department of Chemistry, University of Ulster, Coleraine, Northern Ireland BT52 1SA
Clifford A. Bunton * **and John R. Moffatt**
Department of Chemistry, University of California, Santa Barbara, California 93106, U.S.A.

The $(OC)_3Cr$ π-complexes (**4**) and (**5**) of acyclic and cyclic acetals of tropone undergo acid-catalysed heterolysis in water to give cationic complexes (**2**) and (**6**) that are stable in solutions of pH < *ca.* 5. These cations are thermodynamically more stable than the corresponding uncomplexed alkoxytropylium cations (**8**) and (**13**) but stabilisation is less than that resulting from $(OC)_3Cr$ complexation of the tropylium cation. The spiro-acetals (**5a**—**c**) have very similar reactivities towards heterolysis and are somewhat less reactive than the acyclic acetals (**4a**—**d**). These heterolysis reactions, and their reverse, are *exo*-stereospecific. Reactions of the acyclic acetals with aqueous solutions of high pH give the tropone complex (**9**), the acetal heterolysis step being rate-limiting. The complexed alkoxytropylium cations (**2**) and (**7**) undergo base-catalysed conversion in water into the tropone complex; the intermediate (hydroxy)alkoxy compounds do not build up during these reactions whose rates are relatively insensitive to the identity of the alkoxy group. The reactivity of water relative to that of hydroxide ion towards these cations is much lower than predicted by Swain–Scott and Ritchie nucleophilicity scales. In aqueous alkali, the complexed (hydroxyalkoxy)tropylium cations (**6**) give apparently exclusively the corresponding spiro-acetals (**5**). These acetals and cations co-exist in aqueous solutions of pH 6—7 and their interconversions in these solutions are much faster than formation of the tropone complex. Conversion of the cations (**6**) into the acetals (**5**) is catalysed by borate but not by Tris buffer. Salts speed heterolysis of the acetals (**4**) and (**5**) and inhibit reactions of the cations (**2**), (**6**), and (**7**). Comparisons of reactivities of the $(OC)_3Cr$-complexed diethyl, ethylene, and trimethylene acetals of tropone with those reported earlier for uncomplexed analogues show that complexation does not change the overall pattern of reactivity but suggest that the transition states for heterolysis of the complexed acetals are 'earlier' (more acetal-like).

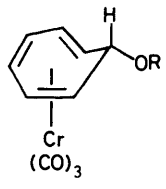
In an earlier paper,[1] the effects of π-complexation with an $(OC)_3M$ group upon the reactivities of the tropylium cation and 7-alkoxycycloheptatrienes were discussed. We now describe kinetic and thermodynamic studies of reactions of $(OC)_3Cr$ π-complexes of acyclic and cyclic tropone acetals and related alkoxytropylium cations.

The overall reactions are shown in the Scheme. We measured rate and equilibrium constants for these transformations in water over a wide pH range and compared these data with those for the corresponding metal-free systems[2,3] in order to assess the effect of metal complexation. For these organometallic substrates, we can also examine stereochemistry and reactivity of acetals with different alkoxy groups and investigate possible build-up of (hydroxy)alkoxy compounds in the formation of the tropone complex (9) from the alkoxytropylium cations.

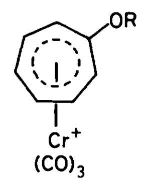


Scheme.

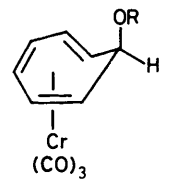
Synthesis of Complexes.—The $(BF_4)^-$ salts of the alkoxytropylium cations (**2a**, **b**) were obtained[4] by hydride-transfer reactions of 7-*endo*-alkoxycycloheptatriene complexes (**1a**, **b**) with trityl $(BF_4)^-$. The crystal structure of (**2a**) $(BF_4)^-$ has established[5] an η^7-mode of attachment of the tropylium ring to the chromium atom. Additions of methoxide ion to the cation (**2a**) and of ethoxide ion to (**2b**) gave the tropone acetal complexes (**4a**) and (**4b**), respectively. These nucleophilic additions are *exo*-stereoselective;[1] thus, ethoxide adds to (**2a**) to give the *exo*-ethoxy-*endo*-methoxy product (**4c**), and the stereoisomer (**4d**) results from addition of methoxide to (**2b**). These acetal complexes and the stereoisomeric ethers (1) and (3) are readily differentiated from their ^1H n.m.r. spectra; the protons of a substituent attached 7-*exo* to the cycloheptatriene ligand are shielded relative to their environment when the same substituent is attached in the 7-*endo* configuration (Table 1). A related stereoselectivity is found for the reverse reactions; treatment of the acetals (4) with protic acid or trityl cation


(1)

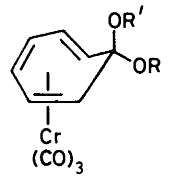
a ; R = Me
b ; R = Et


(2)

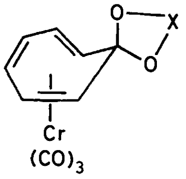
a ; R = Me
b ; R = Et

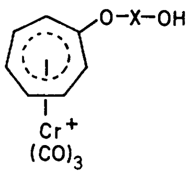

(3)

a ; R = Me
b ; R = Et

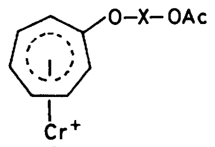

(4)

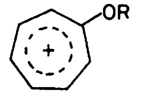
a; R = R′ = Me
b; R = R′ = Et
c; R = Me, R′ = Et
d; R = Et, R′ = Me


(5)

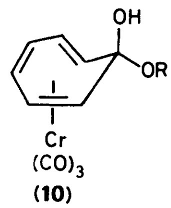

(6)

a; X = $(CH_2)_2$
b; X = $(CH_2)_3$
c; X = CH_2 CH_2

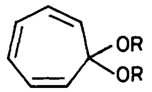

(7)


(8)

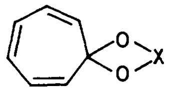
a; R = Me
b; R = Et

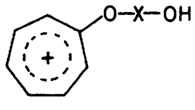

(10)

a; R = Me
b; R = Et


(11)

a; R = Me
b; R = Et


(12)


(13)

a; X = $(CH_2)_2$
b; X = $(CH_2)_3$
c; X = CH_2 CH_2

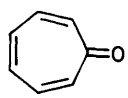

(14)

Table 1. ^1H N.m.r. chemical shifts for protons of 7-alkoxy groups in the complexes (**1**), (**3**), and (**4**)

	δ-values (CS_2 solutions)^a			
Complex	7-*exo*-OMe	7-*endo*-OMe	7-*exo*-OEt	7-*endo*-OEt
(**1a**)		3.33 s		
(**1b**)				1.25 t 3.42 q
(**3a**)	2.95 s			
(**3b**)			0.84 t 3.08 q	
(**4a**)	2.60 s	3.20 s		
(**4b**)			0.81 t 3.04 q	1.24 t 3.50 q
(**4c**)		3.21 s	0.81 t 3.03 q	
(**4d**)	2.62 s			1.33 t 3.48 q

^{a} Against Me_4Si as internal reference; s = singlet, t = triplet, q = quartet.

removes the *exo*-alkoxy group; *i.e.* (**4a**) and (**4c**) are converted into (**2a**) while (**4b**) and (**4d**) give (**2b**).

The complexed spiro-acetals (**5a**—**c**) were obtained by reactions of $(MeCN)_3Cr(CO)_3$ with the free acetals which were synthesised[3] by reactions of the $(BF_4)^-$ salt of ethoxytropylium cation (**8b**) with appropriate diols. Treatment of these complexes with concentrated aqueous HBF_4 in MeCN gave the $(BF_4)^-$ salts of the (hydroxyalkoxy)tropylium cations (**6a**—**c**). When these reactions were conducted in acetic anhydride instead of MeCN, the $(BF_4)^-$ salts of the corresponding acetates (**7a**—**c**) were isolated.

The final product of reactions of the cations (**2**) with water or hydroxide ion is the tropone complex (**9**) which was prepared for identification purposes by the reaction[4] of $(MeCN)_3Cr(CO)_3$ with tropone.

Reactions of Acyclic Acetals (**4**) *and Related Cations* (**2**).—The acetals (**4a**—**d**) undergo heterolysis in aqueous acids by exclusive loss of the *exo*-alkoxy group to give the corresponding alkoxytropylium cations (**2a, b**) which are stable in solutions of pH < *ca.* 5. When the $(BF_4)^-$ salts of these cations are added to aqueous solutions of high pH, the tropone complex (**9**) is formed quantitatively and there is no evidence of build-up of the (presumed) (hydroxy)alkoxy compounds (**10a, b**). The electronic absorption spectra of these complexes should be very similar to those of the acetals (**4**) which are quite distinct from those of the cations (**2**) and the complex (**9**). Continuous monitoring of the progress of the reactions showed smooth spectral changes (**2**) ⟶ (**9**) with at least one tight isosbestic point. Likewise, the

Table 2. Rate constants for heterolysis of the acetals (**4**) in aqueous solutions[a—c]

Acetal	$k_1^{H^+}$/ l mol^{-1} s^{-1}	k_1^{ga}/ l mol^{-1} s^{-1} (buffer)[d]	$k_1^{H_2O}$/s^{-1}
(**4a**)	2.7×10^{4}[e]	8.6 (A)	1.3×10^{-2}
	4.1×10^{4}	8.0 (A)	
	4.5×10^{4}	4.0 (B)	
(**4b**)	6.0×10^{4}	1.1 (B)	3.5×10^{-3}
(**4c**)	3.0×10^{4}	2.2 (B)	5.1×10^{-3}
(**4d**)	1.0×10^{5}	1.9 (B)	9.3×10^{-3}

[a] At 25.0 °C in solutions of constant ionic strength 0.50M (NaCl), unless indicated otherwise. [b] Measured rate constants from which these values are calculated are available in Supplementary Publication 56722. [c] For the uncomplexed acetal (**11b**), the corresponding values (ionic strength, 0.10M) of $k_1^{H^+}$ and $k_1^{H_2O}$ are 2.2×10^{5} l mol^{-1} s^{-1} and 8.6×10^{-3} s^{-1}, respectively (ref. 3*a*). [d] A = acetate buffers (pH 4.7—5.2); B = phthalate buffers (pH 5.2—6.0). [e] In the absence of added NaCl.

$(BF_4)^-$ salts of the (acetoxyalkoxy)tropylium complexes (**7a**—**c**) are converted quantitatively into (**9**) on reaction with aqueous alkali.

The acetals (**4**) are also converted into (**9**) in aqueous solutions of high pH. The (presumed) intermediate cations (**2**) do not build up during these conversions because, as shown later, their reactions with hydroxide ion are much faster than those of their formation by spontaneous heterolysis of the acetals.

Rates of Acetal ⟶ Cation Reactions.—Conversion of the acetals (**4a**—**d**) into the corresponding cations (**2a, b**) by loss of the *exo*-alkoxy group is general acid-catalysed in water. Reactions of (**4a**) with aqueous acetate and phthalate buffers, pH range 4.7—6.0, were followed from the increase in absorption at 310 nm (isosbestic point for cation ⟶ tropone reaction) or 316 nm ($\lambda_{max.}$ for cation). These reactions were first-order and went to completion. Over the pH range studied, conversion of the product cation (**2a**) into the tropone complex (**9**) is sufficiently slow such that this reaction did not interfere. The observed first-order rate constants k_ψ follow equation (1)

$$k_\psi = k_1^{H_2O} + k_1^{H^+}[H^+] + k_1^{ga}[ga] \qquad (1)$$

where ga indicates the acidic component of the buffer, *viz.* acetic acid or phthalate monoanion. Values of k_1^{ga} were calculated from the slopes of plots of k_ψ against [ga] for each pH used, and values of $k_1^{H^+}$ from the extrapolated intercept values (k^{int}; [ga] = 0). For phthalate buffers, with five different pH values, a plot of k^{int} against $[H^+]$ was linear with zero intercept, showing that spontaneous heterolysis ($k_1^{H_2O}$) of the acetal can be neglected under these conditions and $k^{int} = k_1^{H^+}[H^+]$.

These reactions were conducted in solutions of constant ionic strength 0.50M, maintained by addition of NaCl. Reaction was slower in aqueous acetate buffers in the absence of added salt; heterolyses of neutral substrates are accelerated by added salts.[6]

Reactions of the acetals (**4b**—**d**) were studied in phthalate buffers in the presence of NaCl and kinetic behaviours similar to that of (**4a**) were found. Values of the rate constants $k_1^{H^+}$ and k_1^{ga} are in Table 2.

Rates of Acetal ⟶ Tropone Reactions.—At high pH in water, the acetals (**4a**—**d**) are quantitatively converted into the tropone complex (**9**). The intermediate cations (**2a, b**) and the (hydroxy)alkoxy compounds (**10a, b**) do not build up during these reactions and hydronium ion catalysis is negligible; *cf.* for reaction of (**4a**) with aqueous carbonate solution (pH 10.5) of ionic strength 0.50M (NaCl) at 25.0 °C, the observed first-order rate constant for formation of (**9**) is 1.3×10^{-2} s^{-1}, $k_1^{H^+}[H^+]$ for heterolysis of the acetal is 1.5×10^{-6} s^{-1} (Table 2), and $k_2^{HO^-}[HO^-]$ for conversion of (**2a**) into (**9**) is 0.3 s^{-1} (see later).

In the absence of general acid catalysis, therefore, the observed first-order rate constants for the conversion of (**4**) into (**9**) at high pH correspond to $k_1^{H_2O}$ for spontaneous heterolysis of the acetals in water [see equation (1)] and should be insensitive to pH change or base catalysis. We found the same first-order rate constant, within experimental error, for reaction of a given acetal in carbonate or t-butylamine buffers or aqueous NaOH solution, pH range 9.8—11.9, at constant ionic strength. Values of $k_1^{H_2O}$ from experiments conducted in solutions of ionic strength 0.50M (NaCl) are in Table 2. Reactions in solutions of lower ionic strength were slower, as expected (see earlier).

Rates of Cation ⟶ Tropone Reactions.—Additions of the $(BF_4)^-$ salts of the cations (**2a, b**) and (**7a**—**c**) to aqueous alkali give the tropone complex quantitatively. Because the (hydroxy)alkoxy compounds (**10**) do not build up during these reactions, as shown earlier, the rate-limiting step is conversion of cation into the (hydroxy)alkoxy compound by nucleophilic addition of hydroxide ion. Interestingly, reaction of $\{(\eta\text{-tropylium})Cr(CO)_3\}^+$ with hydroxide ion takes a different course, giving a range of products including $(OC)_3Cr$ complexes of ditropyl.[1]

Reactions of (**2a**) in 10^{-5}M HCl with aqueous NaOH (0.002—0.05M) were followed by stopped-flow spectrometry (see Experimental section). These reactions were first-order in (**2a**) and went to completion. The observed first-order rate constants k_ψ varied linearly with $[HO^-]$ ($k_\psi = k_2^{HO^-}[HO^-]$) and, under these conditions, the contribution of water addition to (**2a**) is negligible. Added salts showed these reactions, with the effect of NaCl < NaBr < $NaClO_4$; the rate constant for reaction with 5×10^{-3}M NaOH at 25.0 °C was reduced by factors of two and three, respectively, by 0.50M NaCl and $NaClO_4$.

Reactions of the cations (**2a, b**) and (**7a**—**c**) with water were catalysed by aqueous carbonate, borate, and Tris [*i.e.* $(HOCH_2)_3CNH_2$] buffers, pH 7.9—10.4. All reactions were first-order in cation and went to completion. The first-order rate constants k_ψ incorporate contributions from unassisted addition of water, addition of hydroxide ion, and a buffer base-catalysed reaction [equation (2)]

$$k_\psi = k_2^{H_2O} + k_2^{HO^-}[HO^-] + k_2^{gb}[gb] \qquad (2)$$

where gb indicates the basic component of the buffer. Values of k_2^{gb} were obtained from the slopes of plots of k_ψ against [gb] at each pH. The intercept values (k^{int}; [gb] = 0) of k_ψ varied linearly with $[HO^-]$ and spontaneous water addition can be neglected; values of $k_2^{HO^-}$ were calculated from the slopes. As indicated earlier, the rates of these reactions are sensitive to the ionic strength of the solutions. However, good agreement was found between $k_2^{HO^-}$ values for each of the organometallic cations from experiments with the three buffer systems in solutions of constant ionic strength 0.50M (NaCl).

The first-order rate constants for conversion of the cations (**2**) and (**7**) into the tropone complex (**9**) approach those for spontaneous water addition (*i.e.* $k_2^{H_2O}$) as the pH of the reaction solution is lowered. Addition of the $(BF_4)^-$ salts of these cations to water of pH *ca.* 6 gave (**9**) quantitatively and, as at higher pH, there was no evidence of build-up of intermediate (hydroxy)alkoxy compound. Acid is liberated in these reactions:

$$e.g.\ (\mathbf{2}) + H_2O \longrightarrow (\mathbf{9}) + ROH + H^+$$

with substrate concentrations *ca.* 10^{-5}M, the pH of the solutions fell by 1—2 units over the course of the reactions which nonetheless followed first-order kinetics throughout, showing

Table 3. Rate constants for hydrolysis of the cations (**2**) and (**7**) in aqueous solutions[a—c]

Cation	$k_2^{HO^-}$/ l mol^{-1} s^{-1}	k_2^{gb}/ l mol^{-1} s^{-1} (buffer)[d]	$k_2^{H_2O}$/s^{-1}
(**2a**)	1.0×10^3 1.5×10^{3}[e] 1.8×10^{3}[f]	3.4×10^{-3} (A) 4.1×10^{-2} (B) 0.54 (C)	7.8×10^{-4}
(**2b**)	8.8×10^2	2.5×10^{-3} (A) 5.3×10^{-2} (B) 0.31 (C)	6.0×10^{-4}
(**7a**)	1.1×10^3	2.7×10^{-3} (A) 3.4×10^{-2} (B) 0.54 (C)	8.6×10^{-4}
(**7b**)	9.5×10^2	2.4×10^{-3} (A) 2.2×10^{-2} (B) 0.29 (C)	7.0×10^{-4}
(**7c**)	1.1×10^3	3.1×10^{-3} (A) 2.2×10^{-2} (B) 0.30 (C)	8.4×10^{-4}

[a] At 25.0 °C; values of $k_2^{HO^-}$ and k_2^{gb} are for reactions in solutions of constant ionic strength 0.50M (NaCl), unless indicated otherwise; values of $k_2^{H_2O}$ are for reactions in the absence of added salt. [b] As for Table 2. [c] For the uncomplexed cation (**8b**), the corresponding values (ionic strength, 0.10M) of $k_2^{HO^-}$ and $k_2^{H_2O}$ are 1.0×10^4 l mol^{-1} s^{-1} and 1.7×10^{-2} s^{-1}, respectively (ref. 3*a*). [d] A = Tris buffers (pH 7.9—8.3); B = borate buffers (pH 8.5—9.6); C = carbonate buffers (pH 9.4—10.4). [e] With NaOH and in the absence of NaCl. [f] In 0.025—0.10M carbonate buffer (pH 9.0), and extrapolation to zero [buffer], in the absence of NaCl.

Table 4. Interconversions of spiro-acetals (**5**) and related cations (**6**) in aqueous solution[a]

System	% Cation[b]	pK_{R^+OH}[c]	$10^7K_{R^+OH}$/mol l^{-1}
(**6a**) $\rightleftharpoons$ (**5a**)	40—77	6.60	2.51
(**6b**) $\rightleftharpoons$ (**5b**)	46—82	6.86	1.38
(**6c**) $\rightleftharpoons$ (**5c**)	28—80	6.60	2.51

[a] At 25.0 °C with phosphate buffer (pH range 6—7); 0.50M (NaCl). [b] Range of measured values of relative percentage in solution of (**6**); %(**5**) + %(**6**) = 100; details in Supplementary Publication 56722. [c] From equation (5); see text.

that hydroxide ion addition does not interfere; *cf.* at initial pH 5.74, $k_\psi = k_2^{H_2O} > ca.\ 100\, k_2^{HO^-}[HO^-]$ for all substrates. These experiments were conducted with no added salt; otherwise reaction is so slow that decomposition of the organometallic complexes interferes with the rate measurements. Protonation of the tropone product (**9**) to give the cation (**2**; R = H) did not complicate these experiments; the pK_a value for the conjugate acid of (**9**) in water is *ca.* 1.1.[7]

Values of $k_2^{HO^-}$, k_2^{gb}, and $k_2^{H_2O}$ for reactions of the cations (**2a, b**) and (**7a—c**) are in Table 3.

Reactions of Spiro-acetals (**5**) *and Related Cations* (**6**).—In water of pH < *ca.* 5, the spiro-acetals (**5a—c**) ring-open to give the corresponding cations (**6a—c**) which are stable under these conditions. However, in water of pH *ca.* 7, acetal and cation interconvert, their relative concentrations being pH dependent. The tropone complex (**9**) is formed in these solutions but the reactions are very slow with half-lives of several hours, because the concentration of hydroxide ion is very low, and this reaction cannot be followed to completion; over time, the organometallic substrates decompose in aqueous solution.

Each step in the hydrolysis of the acyclic acetals, *i.e.* (**4**) ⟶ (**2**) ⟶ (**10**) ⟶ (**9**), is irreversible under the experimental conditions used. However, the (hydroxyalkoxy)tropylium cations (**6**) can, in principle, react with water or hydroxide ion either by nucleophilic addition to give intermediates (**10**; R = OH) and thence tropone complex (**9**) or by deprotonation and re-formation of spiro-acetal (**5**). Product isolation experiments were carried out in which the $(BF_4)^-$ salts of the cations (**6a—c**) reacted in aqueous carbonate solutions of pH *ca.* 10.5. There was almost quantitative (*ca.* 95%) recovery of organometallic substrate and, in every case, the ^1H n.m.r. spectrum of the product was identical with that of the spiro-acetal corresponding to the starting cation. The low-field resonances in the spectrum of the tropone complex (**9**) appear at slightly lower field than those of the acetals (**5**) and the spectra of synthetic mixtures of each acetal with small known proportions of (**9**) showed that the presence of 5% of the latter is readily detectable, the lower limit of detection being *ca.* 3%. Therefore, the cations (**6**) react with hydroxide ion preferentially by neighbouring-group participation, *i.e.* by proton loss and spiro-acetal formation, and this reaction is kinetically favoured over hydroxide ion addition to the tropylium ligand by a factor > 20.

Reversibility of Acetal $\rightleftharpoons$ *Cation Reactions.*—Addition of either acetal (**5**) or corresponding cation (**6**) as $(BF_4)^-$ salt to an aqueous phosphate buffer, pH 6—7, rapidly gave a mixture of the two species. Their relative proportions were pH dependent but independent of the identity of the starting material. In these solutions, interconversion of (**5**) and (**6**) is substantially faster than formation of the tropone complex (**9**) from the mixture, such that it is possible to define an 'equilibrium' constant K_{R^+OH} for interconversion of cation and acetal; equations (3)—(5).

$$(\mathbf{6}) + H_2O \rightleftharpoons (\mathbf{5}) + H_3O^+ \qquad (3)$$

$$K_{R^+OH} = \{[(\mathbf{5})][H_3O^+]/[(\mathbf{6})]\}_{equil} \qquad (4)$$

$$pK_{R^+OH} = \log\{[(\mathbf{6})]/[(\mathbf{5})]\}_{equil} + pH \qquad (5)$$

True equilibria are not achieved in these reactions because the component substrates are slowly consumed. For each system, the relative proportions of acetal and cation in a series of phosphate buffer solutions of ionic strength 0.50M (NaCl) were determined from their electronic absorption spectra, those of the organometallic reactants being quite distinct. Plots of the log{[(**6**)]/[(**5**)]} values against −pH were linear and of unit slope and the pK_{R^+OH} values* (Table 4) corresponded to the pH of a solution in which [(**6**)] = [(**5**)].

Identification of Rate Constants.—For the reactions of the spiro-acetals (**5**) and related cations (**6**), the various rate constants are identified as follows:

$$(\mathbf{5}) \underset{k_3^{HO^-}.\ k_3^{gb},\ k_3^{H_2O}}{\overset{k_1^{H^+},\ k_1^{ga},\ k_1^{H_2O}}{\rightleftharpoons}} (\mathbf{6}) \xrightarrow{k_2^{HO^-},\ k_2^{gb},\ k_2^{H_2O}} (\mathbf{10}) \longrightarrow (\mathbf{9})$$

where the superscript H_2O refers to a spontaneous (water-assisted) reaction, H^+ and ga refer to hydronium ion- and buffer acid-catalysed reactions, respectively, and HO^- and gb refer to hydroxide ion- and buffer base-catalysed reactions, respectively; the subscripts 1 and 2 identify the same reactions as for the acyclic acetals (**4**) and related cations (**2**), discussed earlier.

---

* These constants should not be confused with the pK_{R^+} constants conventionally used to characterise carbocation $\rightleftharpoons$ alcohol equilibria in aqueous acidic solutions.

Table 5. Rate constants for interconversions of spiro-acetals (**5**) and related cations (**6**) in aqueous solutions[a—c]

System	$k_1^{H^+}$/ l mol^{-1} s^{-1}	k_1^{ga}/ l mol^{-1} s^{-1} (buffer)[d]	$k_1^{H_2O}$/s^{-1}	$k_3^{HO^-}$/ l mol^{-1} s^{-1}	k_3^{ga}/ l mol^{-1} s^{-1} (buffer)[d]	$k_3^{H_2O}$/s^{-1}
(**5a**) $\rightleftharpoons$ (**6a**)	1.6×10^4	6.2 (A)	6.7×10^{-4}	1.7×10^4	6.0 (B)	4.0×10^{-3}
(**5b**) $\rightleftharpoons$ (**6b**)	1.5×10^4	1.2 (C)	7.5×10^{-4}	1.0×10^4	0.4 (B)	2.0×10^{-3}
(**5c**) $\rightleftharpoons$ (**6c**)	2.9×10^3	0.15 (C)	3.6×10^{-4}	9.1×10^3	0.9 (B)	7.3×10^{-4}

[a] At 25 °C in solutions of constant ionic strength 0.50M (NaCl). [b] As for Table 2. [c] Corresponding values (ionic strength, 0.10M) for the uncomplexed spiro-acetals are: (**12a**), $k_1^{H^+} = 2.1 \times 10^4$ l mol^{-1} s^{-1}, $k_1^{H_2O} = 0.13$ s^{-1}, $k_3^{HO^-} = 8.0 \times 10^7$ l mol^{-1} s^{-1}, $k_3^{H_2O} = 0.13$ s^{-1}; (**12b**), $k_1^{H^+} = 1.8 \times 10^4$ l mol^{-1} s^{-1}, $k_1^{H_2O} = 4.0 \times 10^{-4}$ s^{-1}, $k_3^{HO^-} = 9.4 \times 10^4$ l mol^{-1} s^{-1}, $k_3^{H_2O} = 4.1 \times 10^{-2}$ s^{-1} (ref. 3*b*). [d] A = phthalate buffers (pH 4.9—5.7); B = borate buffers (pH 8.0—9.0); C = acetate buffers (pH 4.4—5.4).

Rates of Acetal ⟶ Cation Reactions.—The cations (**6a**—**c**) are stable in aqueous acid and their formation from the acetals (**5a**—**c**) can be followed. Reactions at low pH were followed in a stopped-flow spectrometer (see Experimental section), mixing equal volumes of a solution of acetal in aqueous NaOH and a solution of aqueous HCl in excess. The ionic strength was 0.50M (NaCl). All reactions went to completion and were first-order in acetal and in H$^+$; $k_\psi = k_1^{H^+}[H^+]$. The rate constants $k_1^{H^+}$ are in Table 5. The contribution of water-assisted acetal ring-opening ($k_1^{H_2O}$) is negligible at low pH.

Buffer catalysis of acetal ring-opening was observed for reactions of (**5a**—**c**) in acetate and phthalate buffers. For each acetal, a pH range was chosen so that there was ⩾ 90% conversion into cation (*cf.* pK_{R^+OH} values, Table 4). The reactions were first-order in acetal and the first-order rate constants k_ψ were corrected for the contribution of the reverse reaction from the relationship:

$$k_f = k_\psi[\%(\mathbf{6})]/100$$

where [%(**6**)], calculated from the appropriate pK_{R^+OH} value [equation (5)], is the proportion of cation in the final product mixture at the reaction pH. The rate constants (Table 5) for hydronium ion and buffer acid catalysis $k_1^{H^+}$ and k_1^{ga}, respectively, were calculated from these k_f values as described earlier [*cf.* equation (1)]. Values of $k_1^{H^+}$ from these experiments agreed with those for the reactions in aqueous HCl. The contribution of the water reaction ($k_1^{H_2O}$) was insignificant in these acidic buffers.

There are positive salt effects on these acetal ring-opening reactions. For example, for reaction of (**5b**) in aqueous acetate buffer, pH 5.1, increase in the ionic strength from 0.10—0.50M by addition of NaCl increases the first-order rate constant from 0.13—0.19 s^{-1}.

Rates of Cation ⟶ Acetal Reactions.—As shown earlier, the cations (**6**) are converted exclusively into the acetals (**5**) on reaction in aqeuous alkali. Reactions of the (BF$_4$)$^-$ salts of the cations were followed in Tris [*i.e.* (HOCH$_2$)$_3$CNH$_2$] and borate buffers, pH 8.0—9.0, at constant ionic strength 0.50M (NaCl). Reactions were first-order and proceeded to >90% completion. The first-order rate constants k_ψ were corrected for the contribution of the reverse reaction from the relationship:

$$k_r = k_\psi[\%(\mathbf{5})]/100$$

where [%(**5**)] is the proportion of acetal in the final product mixture at the reaction pH, calculated from the appropriate pK_{R^+OH} value (Table 4).

These rate constants may include contributions from spontaneous, hydroxide-, and buffer base-catalysed reactions [equation (6)]

$$k_r = k_3^{H_2O} + k_3^{HO^-}[HO^-] + k_3^{gb}[gb] \qquad (6)$$

For reactions in borate buffers, values of k_3^{gb} were obtained from the slopes of plots of k_r against [gb] and values of $k_3^{HO^-}$ from the slopes of plots of intercept values k^{int} ([gb] = 0) against [HO$^-$]. The contribution of the water reaction ($k_3^{H_2O}$) is negligible under these conditions. The rates of reactions with Tris buffers at a fixed pH, however, were insensitive to [buffer], 0.05—0.20M, showing that the amine base is not an effective catalyst of acetalisation. Values of $k_3^{HO^-}$ for these reactions were obtained from the slopes of k_r against [HO$^-$], which again passed through the origin; these agreed with values from the borate buffer reactions.

Values of $k_3^{HO^-}$ and k_3^{gb} from these experiments are in Table 5.

Spontaneous Reactions in Water.—As explained earlier, values of $k_1^{H_2O}$ and $k_3^{H_2O}$ for spontaneous (water-catalysed) interconversion of the spiro-acetals (**5**) and (hydroxyalkoxy)-tropylium cations (**6**) could not be calculated from the rate data for reactions in buffers. However, these rate constants can be estimated from values of $k_1^{H^+}$, $k_3^{HO^-}$, and K_{R^+OH} (Tables 4 and 5) according to the relationships (7) and (8)

$$k_3^{H_2O} = k_1^{H^+} K_{R^+OH} \qquad (7)$$

$$k_1^{H_2O} = k_3^{HO^-} K_w / K_{R^+OH} \qquad (8)$$

where K_w is the ionic product for water. These estimated values, which relate to reactions in aqueous solutions of ionic strength 0.50M, are in Table 5. Their magnitudes fit with the earlier conclusions that the spontaneous reactions make negligible contributions to the reactions in buffers; *e.g.* for reaction of (**5a**) at pH 5, $k_1^{H^+}[H^+] = 240\, k_1^{H_2O}$, and for reaction of (**6a**) at pH 9, $k_3^{HO^-}[HO^-] = 42\, k_3^{H_2O}$.

Rates of Cation ⟶ Tropone Reactions.—It was concluded earlier that, in reactions of the cations (**6**) with hydroxide ion, spiro-acetalisation is strongly favoured over (hydroxy)alkoxy compound formation; *i.e.* $k_3^{HO^-} > 20\, k_2^{HO^-}$ such that values of $k_2^{HO^-}$ must be <*ca.* 9×10^2 l mol^{-1} s^{-1}. In fact, $k_2^{HO^-}$ values of this magnitude were obtained (Table 3) for addition of hydroxide ion to the related cations (**2**) and (**7**) for which acetalisation cannot occur.

In order to convert the cations (**6**) into the tropone complex (**9**), reactions must be conducted in solutions of pH sufficiently low to ensure that the cation is maintained in 'equilibrium' with the corresponding acetal, *i.e.* at a pH around the pK_{R^+OH} value (Table 4) for the system. Mixtures of the cations (**6**) and acetals (**5**) are very slowly converted into (**9**) in phosphate buffers of pH *ca.* 7. However, during such slow reactions (half-lives of several hours), decomposition of the organometallic substrates becomes a serious problem and rate constants could not be determined accurately.

Discussion

Stability Effects.—We have shown[1] earlier that the tropylium cation $(\mathrm{Tr})^+$ is markedly stabilised by π-complexation with the $(\mathrm{OC})_3\mathrm{Cr}$ group, as indicated by the $\mathrm{p}K_{\mathrm{R}^+}$ values for $\{(\eta\text{-Tr})\mathrm{Cr(CO)_3}\}^+$ and $(\mathrm{Tr})^+$ in methanol and in water ($\Delta\mathrm{p}K_{\mathrm{R}^+} > 4$). A similar comparison of the stabilities of the alkoxy-substituted cations (**2**) and (**8**) is less straightforward. For the hypothetical equilibrium of equation (9)

$$(\mathbf{2}) + \mathrm{H_2O} \underset{k_{\mathrm{r}}^{\mathrm{H}^+}}{\overset{k_2^{\mathrm{H_2O}}}{\rightleftharpoons}} (\mathbf{10}) + \mathrm{H}^+ \qquad (9)$$

estimates of the equilibrium constants ($K_{\mathrm{R}^+} = k_2^{\mathrm{H_2O}}/k_{\mathrm{r}}^{\mathrm{H}^+}$) can be made if it is assumed that values of $k_{\mathrm{r}}^{\mathrm{H}^+}$ for (hydroxy)alkoxy compound heterolysis approximate to values of $k_1^{\mathrm{H}^+}$ (Table 2) for acetal heterolysis under the same conditions, values of $k_2^{\mathrm{H_2O}}$ being known (Table 3). On this basis, an estimate of *ca.* 8 can be made for the $\mathrm{p}K_{\mathrm{R}^+}$ value for the cations (**2a**, **b**) in water. The corresponding $k_2^{\mathrm{H_2O}}$ and $k_1^{\mathrm{H}^+}$ values[3a] for ethoxytropylium cation (**8b**) give a $\mathrm{p}K_{\mathrm{R}^+}$ estimate of *ca.* 7. This suggests that, whereas substitution of $(\mathrm{Tr})^+$ by an alkoxy group gives a substantial enhancement of stability in water ($\Delta\mathrm{p}K_{\mathrm{R}^+} > 2$), like substitution of $\{(\eta\text{-Tr})\mathrm{Cr(CO)_3}\}^+$ may in actuality be destabilising, the relative importance of the $-I$ effect being more marked for this system. For 'equilibria' between the (hydroxyalkoxy)tropylium cations (**6a**, **b**) and spiro-acetals (**5a**, **b**) in aqueous solutions, the $\mathrm{p}K_{\mathrm{R}^+\mathrm{OH}}$ values (Table 4) as defined by equation (5) are around 1.4 units more positive than corresponding values calculated from rate constants for the metal-free systems.[3b]

From these comparisons,* it may be concluded that $(\mathrm{OC})_3\mathrm{Cr}$ complexation stabilises alkoxytropylium cations, but less than for tropylium cation.

Acetal Heterolysis.—Hydrolysis of most simple aliphatic acetals follows the *A*1 mechanism with hydronium ion catalysis. It involves pre-equilibrium substrate protonation, and the rate-limiting step is heterolysis of the conjugate acid of the acetal to give an alkoxycarbocation.[8] General acid catalysis of the reaction has been found only for substrates where the basicity of the alkoxy groups is lower than normal and/or where the C–OR bond breaking step is especially favourable.[2,9]

Heterolysis of the acetals (**4a**—**d**) and (**5a**—**c**) is general acid-catalysed as for uncomplexed tropone acetals.[2,3] Spontaneous heterolysis in water was observed only in solutions of high pH where the hydronium ion-catalysed reaction is suppressed. These reactions occur by departure of a poor leaving group and the occurrence of general acid catalysis must be related to the high thermodynamic stabilities of the resulting alkoxycarbocations (**2**) and (**6**). The rate constants k_1^{ga} (Table 2) for heterolysis of the acetal (**4a**) catalysed by acetic acid and phthalate monoanion ($\mathrm{p}K_\mathrm{a}$ values in water, 4.75 and 5.51, respectively) give a Brønsted α-value around 0.4 (neglecting the different charges on these acids), consistent with incomplete proton transfer to the 7-*exo*-alkoxy group in the transition state for heterolysis. Results[1] for heterolysis of the ether (**3a**) in water indicated a more advanced proton transfer in the transition state.

The identity and location (*exo* or *endo*) of the two 7-alkoxy groups (OMe or OEt) have little effect on the reactivity of the acetals (**4a**—**d**). However, there is a consistent leaving group effect on the heterolysis rate constants $k_1^{\mathrm{H}^+}$, k_1^{ga}, and $k_1^{\mathrm{H_2O}}$ (Table 2) for the four acetals; under the same experimental conditions, an *exo*-OMe group departs at a rate *ca.* twice that for an *exo*-OEt group, where these reactions produce the same complexed alkoxytropylium cation.

Differences in the reactivities towards heterolytic ring-opening of the spiro-acetals (**5a**—**c**) are relatively small. Opening of the seven-membered ring in the acetal (**5c**) occurs less readily than for the five- and six-membered spiro-acetals (**5a**, **b**), based on $k_1^{\mathrm{H}^+}$ and $k_1^{\mathrm{H_2O}}$ values (Table 5), but the differences are no greater than a factor of *ca.* 5, probably due to the rigidity imposed by the double bond in the spiro-acetal ring of (**5c**). Unfortunately, we were unable to synthesise for comparison the saturated analogue [**5**; X = $(\mathrm{CH_2})_4$]; attempted catalytic hydrogenation of (**5c**) caused disruption (decomplexation) of the molecule. The acyclic acetals are more reactive than the spiro-acetals ($k_1^{\mathrm{H}^+}$ and $k_1^{\mathrm{H_2O}}$ values; Tables 2 and 5); *e.g.* for the dimethyl (**4a**) and ethylene (**5a**) acetals, the relative $k_1^{\mathrm{H}^+}$ and $k_1^{\mathrm{H_2O}}$ values are *ca.* 3 and 20, respectively. A similar effect was found[2,3] for uncomplexed analogues.

Hydrolysis of Alkoxytropylium Cations.—Conversion of the cations (**2a**, **b**) and (**7a**—**c**) into the corresponding (hydroxy)-alkoxy compounds (**10**) is in general base-catalysed. The intermediacy of the (hydroxy)alkoxy compounds in the formation of the tropone complex (**9**) can only be assumed because they do not build up in solution during reactions either in basic buffers or in aqueous solutions of lower pH where the major pathway is spontaneous addition of water. Loss of alcohol from the (hydroxy)alkoxy compounds must therefore occur extremely readily, even in solutions of low basicity, as found earlier[2,3] for reactions of the uncomplexed alkoxytropylium cations (**8b**) and (**13a**, **b**). The (hydroxyalkoxy)tropylium cations (**6a**—**c**) are not readily converted into the tropone complex (**9**) because reactions with aqueous basic solutions preferentially give spiro-acetal (see later).

The rate constants (Table 3) for addition of hydroxide ion and water to the cations (**2a**, **b**) and (**7a**—**c**) are rather insensitive to the identity of the alkoxy group attached to the reaction site; all the $k_2^{\mathrm{HO}^-}$ values are in the range 10^2 (9.9 ± 1.1) $\mathrm{l\,mol^{-1}\,s^{-1}}$ and the $k_2^{\mathrm{H_2O}}$ values in the range 10^{-4} (7.3 ± 1.3) $\mathrm{s^{-1}}$. The relative reactivities of each of these cations towards hydroxide ion and water are similar, with $\log(k_2^{\mathrm{HO}^-}/k_2^{\mathrm{H_2O}})$ values in the narrow range 6.14 ± 0.03. These log ratios are underestimates, because of differences in ionic strengths of solutions (see earlier), and they show that water is a much less effective nucleophile than would have been expected from the Swain–Scott n and Ritchie N_+ relative nucleophilicity parameters where $\log(k^{\mathrm{HO}^-}/k^{\mathrm{H_2O}}) = 4.2$[10] and 4.5,[11] respectively. Such deviation has been found in other studies; *e.g.* $k^{\mathrm{HO}^-}/k^{\mathrm{H_2O}}$ ratios as high as 10^8 have been reported[12] for additions to aryl- and ferrocenyl-iminium cations.

The rate constants $k_3^{\mathrm{HO}^-}$ for hydroxide-promoted spiro-acetalisation of the cations (**6a**—**c**) in water (Table 5) lie in the range 10^4 (1.3 ± 0.4) $\mathrm{l\,mol^{-1}\,s^{-1}}$, while those ($k_2^{\mathrm{HO}^-}$) for addition of hydroxide ion to the cations (**7a**—**c**) are around 10^3 $\mathrm{l\,mol^{-1}\,s^{-1}}$ (Table 3). Replacement of the acetoxy group in the latter by a hydroxy group should have little effect on the magnitude of these $k_2^{\mathrm{HO}^-}$ values, and so the cations would be expected to undergo preferential spiro-acetalisation in aqueous solutions of high pH, as found in product isolation experiments.

Effects on Rates of Metal Complexation.—The rate constants from this study can be compared with those for hydrolysis of the uncomplexed tropone acetals (**11b**) and (**12a**, **b**).[2,3] Unfortunately, most reactions of these substrates were studied in solutions of lower ionic strength than that used for our work, and there are salt effects on the rates of formation and reaction of alkoxytropylium complexes. There is also a statistical factor to be recognised in direct comparisons of rate constants. The organometallic acetals (**4**) and (**5**) undergo heterolysis

---

* The indicated $\mathrm{p}K_{\mathrm{R}^+}$ differences are are overestimates because of differences in the ionic strengths of solutions for reactions of complexed and uncomplexed systems, as mentioned earlier.

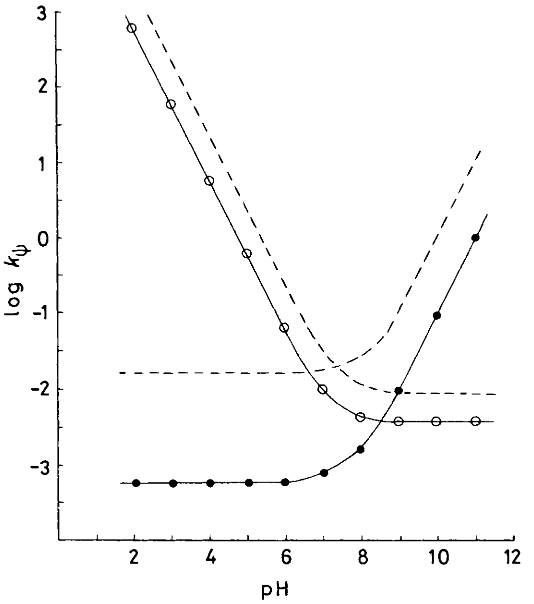


Figure 1. Plots (unbroken lines) of log k_ψ against pH for the reactions (**4b**) ⟶ (**2b**) (open circles) and (**2b**) ⟶ (**9**) (filled circles) in aqueous solutions at 25.0 °C and ionic strength 0.50M in the absence of buffer catalysts; the broken lines are the corresponding plots (ionic strength, 0.10M) for the reactions (**11b**) ⟶ (**8b**) and (**8b**) ⟶ (**14**), from the rate constant data in ref. 3*a*. No correction has been made for the statistical factor (see text); similarly, for Figures 2 and 3

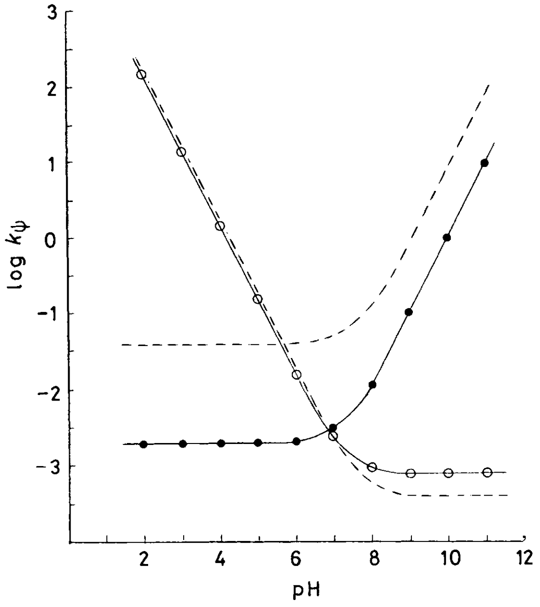


Figure 3. Plots (unbroken lines) of log k_ψ against pH for the reactions (**5b**) ⟶ (**6b**) (open circles) and (**6b**) ⟶ (**5b**) (filled circles) in aqueous solutions at 25.0 °C and ionic strength 0.50M, in the absence of buffer catalysts; the broken lines are the corresponding plots (ionic strength, 0.10M) for the reactions (**12b**) ⟶ (**13b**) and (**13b**) ⟶ (**12b**), from the rate constant data in ref. 3*b*

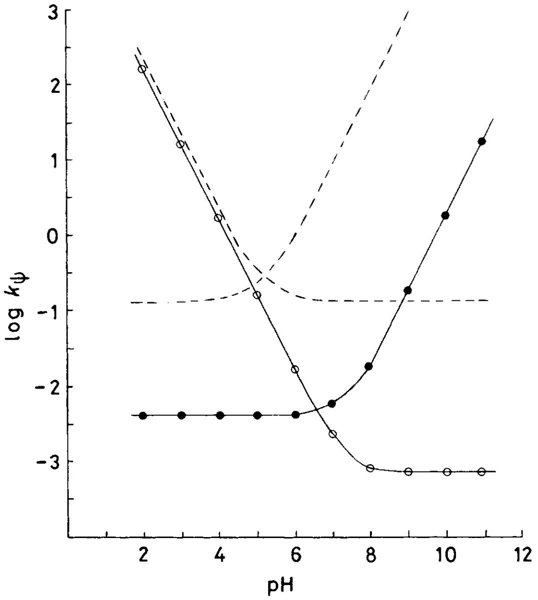


Figure 2. Plots (unbroken lines) of log k_ψ against pH for the reactions (**5a**) ⟶ (**6a**) (open circles) and (**6a**) ⟶ (**5a**) (filled circles) in aqueous solutions at 25.0 °C and ionic strength 0.50M, in the absence of buffer catalysts; the broken lines are the corresponding plots (ionic strength, 0.10M) for the reactions (**12a**) ⟶ (**13a**) and (**13a**) ⟶ (**12a**), from the rate constant data in ref. 3*b*

exclusively by breaking of the *exo* C–O bond, whereas both C–O bonds of the uncomplexed acetals (**11**) and (**12**) have the same reactivity. Likewise, nucleophilic addition to cations such as (**8**) and (**13**) occurs with equal ease to either face of the tropylium ring, whereas the organometallic analogues (**2**) and (**6**) react exclusively from the *exo*-direction.

Overall, the diethyl acetal of tropone (**11b**) and its $(OC)_3Cr$ complex (**4b**) have similar reactivites. Figure 1 shows (log k_ψ)-pH profiles for reactions of these systems in water in the absence of buffer catalysts. The difference is largest for reactions of the uncomplexed cation (**8b**) and its complex (**2b**) with water and hydroxide ion, reflecting the greater thermodynamic stability of the complexed cation. For the organometallic system, in solutions of pH $<$ *ca.* 7 the acetal ⟶ cation reaction is virtually complete before conversion of the cation into the tropone complex (**9**) has become significant; in solutions of pH $>$ *ca.* 10 the cation ⟶ tropone complex reaction is so much faster than the acetal ⟶ cation reaction that the cation does not build up in solution during conversion of acetal into tropone complex, as observed experimentally. The rates of the two reactions are equal at pH *ca.* 8.5, *i.e.*, around one unit higher than that for reaction of the uncomplexed acetal (**11b**). The (log k_ψ)-pH profiles for the other acyclic organometallic acetals (**4a**, **c**, **d**) are very similar to that for (**4b**).

Comparison of the effects of $(OC)_3Cr$ complexation upon the rates of spiro-acetal $\rightleftharpoons$ (hydroxyalkoxy)tropylium cation interconversions for the five-membered (**5a**), (**12a**) and six-membered (**5b**), (**12b**) ring systems are shown by (log k_ψ)-pH profiles in Figures 2 and 3, respectively, for reactions in water in the absence of buffer catalysts. A direct comparison of the organometallic systems (**5a**, **b**) is not shown but the profiles are closely similar, the largest difference (by *ca.* 0.5 log unit) arising from the lower reactivity of the cation (**6b**) as compared with (**6a**) in spontaneous (water-catalysed) spiro-acetalisation.

For the (hydroxyalkoxy)tropylium cation ⟶ spiro-acetal reactions, the organometallic substrates (**6a**, **b**) are much less reactive than are the corresponding uncomplexed cations (**13a**, **b**) in both spontaneous and hydroxide-promoted reactions, because of the greater thermodynamic stabilities of the former. A similar effect (Figure 1) upon rates of *addition* of water and hydroxide ion to the alkoxytropylium cations (**2b**) and (**8b**) was noted earlier. The most striking difference between the sensitivity to complexation of the ethylene and trimethylene systems is in the acetal ring-opening reactions. Complexation has a relatively small effect (Figure 3) for the trimethylene acetals, but the uncomplexed ethylene acetal (**12a**) is very much more reactive than its $(OC)_3Cr$ complex (**5a**) towards spontaneous ring-opening in solutions of high pH (Figure 2) where the contribution of the acid-catalysed reaction is minimal. This difference arises mainly from the large difference (325-fold)[3b] in the reactivities of the uncomplexed acetals (**12a**, **b**) towards spontaneous ring-opening, whereas their complexes (**5a**, **b**) have very similar reactivities (*cf.* $k_1^{H_2O}$ values in Table 5).

This difference in the reactivities of the uncomplexed spiro-acetals has been attributed[3b] to a much 'later' transition state (more advanced C–O bond-breaking) for the spontaneous than for the acid-promoted ring-opening reaction, such that relief of ring strain enhances the reactivity of the five- over that of the six-membered spiro-acetal in the former case. The similarity in the reactivities of the complexes (**5a**, **b**) towards both spontaneous and acid-promoted ring-opening is indicative of 'early' transition states for both processes, with little C–O bond-breaking in either case.

Application of the Hammond Postulate to carbocation forming heterolyses indicates that, for a given reaction of a series of related substrates, the position of the transition state would be 'earlier' for those reactions that lead to more stable carbocations; evidence on heterolyses of ortho esters supports this hypothesis.[13] In relation to this work, an 'earlier' transition state is indicated for heterolysis of the organometallic acetals than for their uncomplexed analogues, given the greater thermodynamic stabilities of the resulting $(OC)_3Cr$-complexed alkoxytropylium cations. For the reverse reactions [*i.e.* spiro-acetalisation and (hydroxy)alkoxy compound formation], it follows that the transition states for reactions of the organometallic cations would be 'later' than for corresponding uncomplexed cations.

Experimental

For general remarks, see ref. 1.

Preparation of Substrates.—The salts (**2a**)$(BF_4)^-$, (**2b**)-$(BF_4)^-$, and acetal (**4a**), and the tropone complex (**9**) were prepared according to the literature methods.[4]

Tricarbonyl(η-7,7-*diethoxycycloheptatriene*)*chromium* (**4b**).—This compound was prepared as described for (**4a**)[4] by the reaction of (**2b**)$(BF_4)^-$ with NaOEt in ethanol, and was obtained in 64% yield as orange crystals, m.p. 113—114 °C; $\delta(CS_2)$ 0.8 and 1.3 (3 H and 3 H, 2 × t, Me), 3.0 (2 H, q, OCH_2), 3.2—3.9, 4.6—5.1, and 5.5—5.9 (4 H, 2 H, and 2 H, respectively, 3 × m, OCH_2 and vinyl protons) (Found: C, 53.3; H, 5.2. $C_{14}H_{16}CrO_5$ requires C, 53.2; H, 5.1%).

Tricarbonyl(η-7-exo-*ethoxy*-7-endo-*methoxycycloheptatriene*)*chromium* (**4c**).—This compound was prepared as described for (**4a**)[4] by the reaction of (**2a**)$(BF_4)^-$ with NaOEt in ethanol, and was obtained in 58% yield as orange crystals, m.p. 99.5—100.5 °C; $\delta(CS_2)$ 0.8 (3 H, t, Me), 2.9 (2 H, q, OCH_2), 3.2 (3 H, s, OMe), 3.5—3.8, 4.55—5.15, and 5.35—5.95 (each 2 H, 3 × m, vinyl protons) (Found: C, 51.8; H, 4.8. $C_{13}H_{14}CrO_5$ requires C, 51.7; H, 4.6%).

Tricarbonyl(η-7-endo-*ethoxy*-7-exo-*methoxycycloheptatriene*)*chromium* (**4d**).—This compound was prepared as described for (**4a**)[4] by the reaction of (**2b**)$(BF_4)^-$ with NaOMe in methanol, and was obtained in 71% yield as orange needles, m.p. 109.5—110.5 °C; $\delta(CS_2)$ 1.25 (3 H, t, Me), 2.62 (3 H, s, OMe), 3.2—3.9, 4.6—5.15, and 5.4—5.9 (4 H, 2 H, and 2 H, respectively, 3 × m, OCH_2 and vinyl protons) (Found: C, 52.0; H, 4.8. $C_{13}H_{14}CrO_5$ requires C, 51.7; H, 4.6%).

Cycloheptatrienone cis-*but-2-enylene acetal* (**12c**). This compound was prepared as described for the corresponding ethylene and trimethylene acetals[14] by the reaction of (**8b**)$(BF_4)^-$ with *cis*-but-2-ene-1,4-diol and was obtained in 13% yield as a colourless liquid which was used without purification for the synthesis of its $(OC)_3Cr$ complex; $\delta(CDCl_3)$ 4.25 (4 H, s, CH_2), 5.5—6.0 and 6.2—6.9 (each 4 H, 2 m, vinyl protons).

Preparation of Spiro-acetal Complexes (**5**).—The following general procedure was used. A solution of the cycloheptatrienone spiro-acetal (*ca.* 10 mmol) in dry tetrahydrofuran (*ca.* 40 ml) was added to a flask containing an equimolar amount of freshly prepared $(MeCN)_3Cr(CO)_3$ and the mixture was heated under reflux with stirring for 2—4 h under an atmosphere of dry, oxygen-free nitrogen. The solvent was then evaporated under reduced pressure and the residue was extracted with hot hexane, pentane, or ether (as appropriate) giving the product, which was purified by recrystallisation. The following complexes were obtained by this method.

Tricarbonyl(η-*cycloheptatrienone ethylene acetal*)*chromium* (**5a**). This compound was prepared from (**12a**) in 65% yield as orange-red crystals, m.p. 146—147 °C; $\delta(CS_2)$ 3.5—4.2 (6 H, m, CH_2CH_2 and two vinyl protons), 4.7—5.3 and 5.6—6.0 (each 2 H, 2 × m, vinyl protons) (Found: C, 50.1; H, 3.7. $C_{12}H_{10}CrO_5$ requires C, 50.3; H, 3.5%).

Tricarbonyl(η-*cycloheptatrienone trimethylene acetal*)*chromium* (**5b**). This compound was prepared from (**12b**) in 63% yield as a viscous red oil which could not be crystallised; $\delta(CS_2)$ 1.6—1.95 (2 H, m, CH_2), 3.8—4.1 (4 H, m, OCH_2), 5.7—6.0 and 6.3—6.9 (2 H and 4 H, respectively, 2 m, vinyl protons).

Tricarbonyl(η-*cycloheptatrienone*-cis-*but*-2-*enylene acetal*)-*chromium* (**5c**). This compound was prepared from (**12c**) in 68% yield as red crystals, m.p. 159.5—160.5 °C; $\delta(CS_2)$ 3.65—4.05 (4 H, m, OCH_2), 4.15—4.4, 4.6—5.1, and 5.4—5.9 (2 H, 2 H, and 4 H, respectively, 3 m, vinyl protons) (Found: C, 54.0; H, 4.1. $C_{14}H_{12}CrO_5$ requires C, 53.9; H, 3.9%).

Preparation of (*Hydroxyalkoxy*)*tropylium Salts* (**6**)$(BF_4)^-$.—The following general procedure was used. Tetrafluoroboric acid (40% w/v in water; 1.0 ml) was added with cooling to a stirred solution of acetal complex (**5**) (*ca.* 2 mmol) in acetonitrile (5 ml). The solution was then diluted with ether and the precipitated salt was collected and washed thoroughly with ether. The salts were purified by crystallisation from acetone–ether. The following salts were obtained by this method.

Tricarbonyl[η-(2-*hydroxyethoxy*)*tropylium*]*chromium tetrafluoroborate* (**6a**)$(BF_4)^-$. This salt was obtained from (**5a**) in 89% yield as a dark orange powder, m.p. 131—133 °C; $\delta[(CD_3)_2CO]$ 3.8 (1 H, br s, OH), 4.0 and 4.6 (each 2 H, 2 t, OCH_2), 6.35—6.8 and 6.85—7.25 (4 H and 2 H, respectively, 2 × m, ring protons) (Found: C, 38.7; H, 3.1. $C_{12}H_{11}BCrF_4O_5$ requires C, 38.5; H, 3.0%).

Tricarbonyl[η-(3-*hydroxypropoxy*)*tropylium*]*chromium tetrafluoroborate* (**6b**)$(BF_4)^-$. This salt was obtained from (**5b**) in 81% yield as an orange-red powder, m.p. 118—120 °C; $\delta[(CD_3)_2CO]$ 2.0—2.4 (2 H, m, CH_2), 3.3 (1 H, br s, OH), 3.8 and 4.65 (each 2 H, 2 × t, OCH_2), 6.3—6.8 and 6.85—7.35 (4 H and 2 H, respectively, 2 × m, ring protons) (Found: C, 40.4; H, 3.6. $C_{13}H_{13}BCrF_4O_5$ requires C, 40.3; H, 3.4%).

Tricarbonyl[η-(cis-4-*hydroxybut-2-enyloxy*)*tropylium*]-*chromium tetrafluoroborate* (**6c**)$(BF_4)^-$. This salt was obtained from (**5c**) in 83% yield as a dark red gum which could not be induced to crystallise. The salt was rather unstable in the usual n.m.r. solvents and the peaks in the spectra were broadened; $\delta[(CD_3)_2CO]$ 3.5 (1 H, br s, OH), 4.1—4.5 and 5.0—5.3 (each 2 H, 2 × m, OCH_2), 5.7—6.05 (2 H, m, vinyl protons), 6.3—6.8 and 6.8—7.2 (4 H and 2 H, respectively, 2 × m, ring protons).

Preparation of (Acetoxyalkoxy)tropylium Salts (**7**)$(BF_4)^-$.—When the preceding reactions of the acetals (**5**) with tetrafluoroboric acid were carried out in acetic anhydride as solvent in place of acetonitrile, the following ester salts were obtained.

Tricarbonyl[η-(2-*acetoxyethoxy*)*tropylium*]*chromium tetrafluoroborate* (**7a**) $(BF_4)^-$. This salt was obtained from (**5a**) in 73% yield as an orange-red gum which could not be crystallised; δ[$(CD_3)_2CO$] 2.05 (3 H, s, COMe), 4.3—4.95 (4 H, m, OCH_2), 6.3—6.8 and 6.85—7.3 (4 H and 2 H, respectively, 2 m, ring protons).

Tricarbonyl[η-(3-*acetoxypropoxy*)*tropylium*]*chromium tetrafluoroborate* (**7b**)$(BF_4)^-$. This salt was obtained from (**5b**) in 70% yield as a red gum which could not be crystallised; δ[$(CD_3)_2CO$] 2.0—2.6 (5 H, overlapping s and quintet, COMe and CH_2), 4.2—4.7 (4 H, m, OCH_2), and 5.9—7.0 (6 H, m, ring protons).

Tricarbonyl[η-(cis-4-*acetoxybut-2-enyloxy*)*tropylium*]-*chromium tetrafluoroborate* (**7c**)$(BF_4)^-$. This salt was obtained from (**5c**) in 76% yield as an orange gum which could not be crystallised; δ[$(CD_3)_2CO$] 2.0 (3 H, s, COMe), 4.5—4.9 and 5.05—5.35 (each 2 H, 2 m, OCH_2), 5.6—6.1 (2 H, m, vinyl protons), 6.2—6.6 and 6.7—7.2 (4 H and 2 H, respectively, 2 × m, ring protons).

Product Isolation Experiments.—(a) Each of the acetals (**4a**—**d**) (100 mg) was added to an aqueous carbonate buffer solution (50 ml) of pH 10.5 and the mixture was stirred for 40 min. Extraction of the solution with ether gave in each case the tropone complex (**9**) quantitatively, identified by comparison with an authentic sample.[4] Similar experiments in which the $(BF_4)^-$ salts of the cations (**2a, b**) and (**7a**—**c**) were treated with aqueous carbonate buffer also gave the complex (**9**) as the sole product.

(b) The salt (**6a**)$(BF_4)^-$ (100 mg) was added to an aqueous solution (50 ml) of Tris buffer of concentration 0.20M and pH 8.4. The mixture was stirred for 15 min and then extracted exhaustively with ether. The total product (96%) isolated from this extract was identical with the acetal (**5a**). Similar reactions of the $(BF_4)^-$ salts of the cations (**6b**) and (**6c**) gave the corresponding acetals (**5b**) and (**5c**), respectively, in high yields (>95%) as the exclusive products. The ^1H n.m.r. spectra of the products of these reactions were identical with those of the pure acetals. The corresponding spectra of synthetic mixtures of these acetals with known amounts of the tropone complex (**9**) showed that *ca.* 3% of the latter is detectable.

(c) Addition of the acetals (**5**) to aqueous phosphate buffers of pH 6—7 gave solutions in which the tropone complex (**9**) was formed in extremely slow reactions and could be isolated. During the course of these reactions, decomposition of the organometallic substrates occurred as a side-reaction to give absorbing species whose presence interfered with determination of rates of reaction.

Interconversion of Acetals (**5**) *and Cations* (**6**).—A series of seven phosphate buffers spanning the pH range 6—7 was prepared; in each case, the buffer concentration was 0.20M and the ionic strength of the solutions was adjusted to 0.50M by addition of appropriate concentrations of NaCl. To each buffer solution (exactly 2.5 ml) in a 1 cm cuvette, thermostatted at 25.0 °C, was added by micro-syringe an accurate volume (25 μl) of a stock solution (10^{-2}M) of (**6a**)$(BF_4)^-$ in acetonitrile, the solution mixed thoroughly, and the u.v.–visible spectrum recorded every 15 s until the absorbance at 314 nm had stabilised (no longer than a few min). The absorbance value for each buffer pH was noted. The same volume of stock solution was then added separately to 2.5 ml of solutions of aqueous HCl (2.0M) and aqueous carbonate buffer (pH 10.1) at 25.0 °C and the 314 nm absorbance values for 100% cation and 100% acetal, respectively, were noted. From these absorbance values, the relative proportions of cation and acetal in each buffer solution were calculated from the Beer–Lambert law. The entire procedure was then repeated with the acetal (**5a**) in place of the salt (**6a**)$(BF_4)^-$. Within experimental error, the same proportions of (**5a**) and (**6a**) were formed at each pH, irrespective of starting material.

The same sets of experiments were carried out for the acetal/salt pairs (**5b**)/(**6b**)$(BF_4)^-$ and (**5c**)/(**6c**)$(BF_4)^-$. The results from all of these experiments are given in the Supplementary Material.*

From each of these sets of data, plots of log([**6**]/[**5**]) against −pH were linear with slopes close to unity. The pK_{R^+OH} values [see equation (5)] were taken as the pH values on the least-squares best-fit lines of exactly unit slope where log([**6**]/[**5**]) = 0. These results are in Table 4.

Rate Measurements.—For descriptions of the methods used for rate measurements, see ref. 1. All the kinetic measurements were made in water, generally at ionic strength 0.50M (NaCl) although a few experiments were made with no added salt to establish quantitatively the nature of the salt effects. Conditions were chosen to ensure that all reactions were first-order. The faster reactions were followed by rapidly mixing equal volumes of reactant solutions in a stopped-flow spectrometer with acetal in 2 × 10^{-5}M NaOH and the appropriate excess of aqueous HCl. Reactions were followed at the wavelengths: 360 nm, disappearance of acetal; 310 nm (isosbestic point), conversion of acetal into cation and tropone complex; 314—316 nm, formation or disappearance of cation; 325 nm, formation of tropone complex. Tables of first-order rate constants k_ψ from all the experiments are available as Supplementary Material. Derived rate constants were calculated as indicated in the text and are in Tables 2, 3, and 5. Estimates of rate constants were based on measured pH of reaction solutions, literature values of buffer pK_a values (HOAc, 4.75; phthalate monoanion, 5.51; $TrisH^+$, 8.24; H_3BO_3, 9.14; HCO_3^-, 10.25), and a value of 10^{-14} for the autoprotolysis rate constant K_w. No corrections were made for salt effects on dissociation constants.

Acknowledgements

Support of this work by the National Science Foundation (Chemical Dynamics) and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged. N. T. L. thanks the Department of Education (Northern Ireland) for the award of a postgraduate research studentship.

References

1 K. Lal, N. T. Leckey, W. E. Watts, C. A. Bunton, M. M. Mhala, and J. R. Moffatt, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1091.

2 E. Anderson and T. H. Fife, *J. Am. Chem. Soc.*, 1969, **91**, 7163; T. H. Fife and E. Anderson, *J. Org. Chem.*, 1971, **36**, 2357.

3 (*a*) R. A. McClelland and M. Ahmad, *J. Am. Chem. Soc.*, 1978, **100**, 7027; (*b*) R. A. McClelland, M. Ahmad, and G. Mandrapilias, *ibid.*, 1979, **101**, 970.

4 P. L. Pauson and K. H. Todd, *J. Chem. Soc. C*, 1970, 2315, 2638.

5 U. Behrens, J. Kopf, K. Lal, and W. E. Watts, *J. Organomet. Chem.*, 1984, **276**, 193.

6 (*a*) M. J. Postle and P. A. H. Wyatt, *J. Chem. Soc., Perkin Trans. 2*, 1972, 474; (*b*) C. A. Bunton and S. K. Huang, *J. Am. Chem. Soc.*, 1972, **94**, 3436; (*c*) C. A. Bunton, N. Carrasco, and W. E. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1267.

---

* Supplementary material (Supp. No. 56722, pp.38) has been deposited at the British Library Document Supply Centre (Boston Spa).

7 K. Lal, N. T. Leckey, and W. E. Watts, *J. Organomet. Chem.*, 1983, **254**, 193; 1983, **258**, 205.

8 E. H. Cordes, *Prog. Phys. Org. Chem.*, 1967, **4**, 1; T. H. Fife, *Acc. Chem. Res.*, 1972, **5**, 264; E. H. Cordes and H. G. Bull, *Chem. Rev.*, 1974, **74**, 581.

9 T. H. Fife and L. K. Jao, *J. Am. Chem. Soc.*, 1968, **90**, 4081; T. H, Fife and L. Brod, *ibid.*, 1970, **92**, 1681.

10 C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, 1953, **75**, 141.

11 C. D. Ritchie, *Acc. Chem. Res.*, 1972, **5**, 348.

12 E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.*, 1963, **85**, 2843; K. Koehler, W. Sandstrom, and E. H. Cordes, *ibid.*, 1964, **86**, 2413; C. A. Bunton, F. Davoudzadeh, M. H. Jagdale, and W. E. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1984, 395.

13 H. G. Bull, K. Koehler, T. C. Pletcher, J. J. Ortiz, and E. H. Cordes, *J. Am. Chem. Soc.*, 1971, **93**, 3002.

14 H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.*, 1967, **89**, 5208.

Received 14*th March* 1988; *Paper* 8/01023