The Relative Electrophilic Reactivities of Tropylium Cation and its $(OC)_3M$ π-Complexes: Kinetic Studies of Alkoxide Transfer and Reversible Nucleophilic Addition

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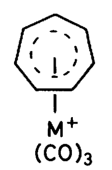
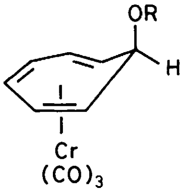
π-Complexation of the tropylium cation $(Tr)^+$ with an $(OC)_3Cr$ group increases thermodynamic stability (ΔpK_{R^+} *ca.* 4.3 in methanol) and reduces reactivity towards abstraction of methoxide ion from Malachite Green methyl ether (MG)OMe ($k^{rel.}$ *ca.* 110) in $MeNO_2$–MeCOEt (40:60 v/v) and nucleophilic *exo*-addition of methanol ($k^{rel.}$ *ca.* 2 100) in methanol. The organometallic cation (**1a**) is stable in aqueous solutions of pH < *ca.* 6, but at higher pH is converted irreversibly into $(OC)_3Cr$ complexes (**5**) and (**6**) of ditropyl. The same complexes are formed on reaction of (**1a**) with 1,8-bis(dimethylamino)naphthalene. The relative rates of transfer of methoxide ion from (MG)OMe to $\{(\eta\text{-Tr})Cr(CO)_3\}^+$, $\{(\eta\text{-Tr})Mo(CO)_3\}^+$, and $\{(\eta\text{-Tr})W(CO)_3\}^+$ in $MeNO_2$–MeCOEt (40:60 v/v) are 1:10:6, respectively. The rates of transfer to $(Tr)^+$ of alkoxide ion from (η-7-*exo*-alkoxycycloheptatriene)$Cr(CO)_3$ complexes (**2a**—**d**) in MeCN decrease through the series: alkoxy = methoxy > ethoxy > isopropoxy > t-butoxy, but the overall rate change is only about five-fold. In methanol, the 7-*exo*-methoxycycloheptatriene complex (**2a**) is about ten times more reactive towards acid heterolysis than is methyl tropyl ether. This conversion is general acid-catalysed. In aqueous solutions of pH > *ca.* 6, the rate of spontaneous heterolysis of the ether (**2a**) is substantially faster than that of consumption of the resulting cation (**1a**) which increases with increasing pH. The 7-*endo*-methoxy stereoisomer (**3**) is inert to acid heterolysis in aqueous solutions to give the cation (**1a**), but undergoes decomplexation to give $(Tr)^+$.

The chemical reactivities of neutral π-hydrocarbons are often changed substantially by complexation with a transition metal.[1] For example, the effects on reactivity of π-complexation of benzenoid[2] and pentafulvenoid[3] compounds with neutral and charged metal–ligand groups are well documented. While there have been extensive studies[4] of the relative electrophilic reactivities of cationic hydrocarbon–metal π-complexes, particularly with regard to metal dependency, much less information is available on the effects of metal complexation upon the reactivities of organic carbocations; most systems that form stable π-complexes with metal–ligand groups (*e.g.*, allyl, dienyl, and polyenyl cations) are themselves too reactive towards nucleophiles to allow direct measurement of rates of reaction.

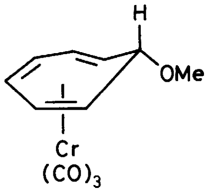
One system that does offer potential for comparative rate measurements is the tropylium cation $(Tr)^+$. Rates of addition of a variety of nucleophiles to this cation and some derivatives have already been reported,[5] and a range of organometallic complexes of the type $\{(\eta\text{-Tr})ML_n\}^+$ is known.[1] Of these, the most readily accessible in stable salts are the cations (1) and, in this paper, we report kinetic studies of the relative electrophilic reactivities of $(Tr)^+$ and its $(OC)_3M$ complexes (M = Cr, Mo, W). Some preliminary results have been published.[6] We have also previously reported[7] a related study of the effect of complexation upon the acid strengths of hydroxytropylium cations (*i.e.*, protonated tropones).



(**1**)
a ; M = Cr
b ; M = Mo
c ; M = W

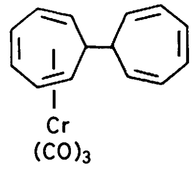


(**2**)
a ; R = Me
b ; R = Et
c ; R = Pr^i
d ; R = Bu^t

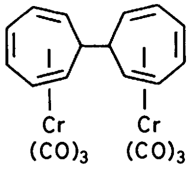


(**3**)

$PhC(OR)Ar_2$
(**4**)
a ; R = Me
b ; R = Et
Ar = $p\text{-}Me_2NC_6H_4$



(**5**)



(**6**)

Synthetic Methods.—Methods of synthesis of $(BF_4)^-$ salts of the cations (**1a**—**c**) and $(Tr)^+$ have been described previously (see Experimental section). The 7-*exo*-alkoxycycloheptatriene complexes (**2a**—**d**) were obtained by reactions of the salt (**1a**) $(BF_4)^-$ with sodium alkoxides, known[8b] to be *exo*-stereoselective. Corresponding 7-*endo*-alkoxycycloheptatriene complexes, *e.g.* (3), can be obtained[8c] by reactions of 7-alkoxycycloheptatrienes with $M(CO)_6$ or, more conveniently, $(MeCN)_3M(CO)_3$. The ethers (**4a,b**) were prepared by the reactions of the oxalate salt of Malachite Green $(MG)^+$ with sodium alkoxides.

Alkoxide-transfer Reactions.—Whereas (7-*endo*-alkoxycycloheptatriene)metal complexes, *e.g.* (3), react with trityl cation by hydride transfer to give the corresponding complexed tropylium cations,[8d] the 7-*exo*-alkoxy isomers (2) undergo alkoxide transfer. This is an example of a general reaction [equation (i)] of potentially wide application.

$$(\mathrm{R}^1)^+ + (\mathrm{R}^2)\mathrm{OR} \rightleftharpoons (\mathrm{R}^1)\mathrm{OR} + (\mathrm{R}^2)^+ \qquad \text{(i)}$$

The direction of such alkoxide-transfer reactions, in principle reversible, is controlled by the relative thermodynamic stabilities of the participating carbocations. The driving force for the fast and essentially quantitative reaction of equation (ii) is the much greater stability of the organometallic cation (**1a**) over that of the trityl cation.

$$\mathrm{Ph_3C^+} + (\mathbf{2}) \longrightarrow \mathrm{Ph_3COR} + (\mathbf{1a}) \qquad \text{(ii)}$$

However, if the stability of the triarylmethyl cation is sufficiently enhanced by introduction of strongly electron-donating substituents (*e.g.*, p-NMe$_2$) into the phenyl rings, then the reaction can be driven in the reverse direction. Thus, it was found that the ethers (**4**) react with (Tr)$^+$ and its (OC)$_3$M complexes (**1**) with formation of the bis(dimethylaminophenyl)-phenylmethyl cation, *i.e.* Malachite Green (MG)$^+$, and that the rates of these alkoxide-transfer reactions [equation (iii)] are conveniently measurable. The relative rates of these alkoxide-transfer reactions, conducted under the same experimental conditions, provide an indication of the relative electrophilic reactivities of the various carbocations.

$$(\mathrm{R}^1)^+ + (\mathrm{MG})\mathrm{OR} \longrightarrow (\mathrm{R}^1)\mathrm{OR} + (\mathrm{MG})^+ \qquad \text{(iii)}$$
$$(\mathrm{R}^1)^+ = (\mathrm{Tr})^+, (\mathbf{1a}\text{—}\mathbf{c})$$

Likewise, it was found that (Tr)$^+$ abstracts alkoxide from the complexed *exo*-ethers (**2a—d**) to give the cation (**1a**) [equation (iv)]. Comparison of the rates of these reactions gives some insight into the importance, or otherwise, of steric crowding in the transition state for alkoxide transfer.

$$(\mathrm{Tr})^+ + (\mathbf{2}) \longrightarrow (\mathrm{Tr})\mathrm{OR} + (\mathbf{1a}) \qquad \text{(iv)}$$

Rate measurements. It was difficult to find a solvent in which the rates of all the reactions of equation (iii) could be measured. Neat solvents such as MeCN, MeNO$_2$, and Me$_2$CO were unsatisfactory either because of insufficient solubility of reactants or because of decomposition of the organometallic substrates (particularly the Mo and W complexes) during the slower reactions. A solvent mixture of MeNO$_2$ and MeCOEt (40:60 v/v) was finally chosen to minimise these problems. Reactions were carried out at 25.0 °C with a large molar excess ($\geqslant$ 100-fold) of the cations, as the (BF$_4$)$^-$ salts, over (MG)OMe (2×10^{-5}M) and their progress was followed by observing the increase in absorption due to (MG)$^+$ at 618 nm, at which wavelength the absorbances of the organometallic substrates are negligible.

A change of solvent was necessary for study of the rates of reactions of the ethers (**2a—d**) with (Tr)$^+$ [equation (iv)] which were followed in MeCN at 25.0 °C by observing the increase in absorption at 316 nm resulting from formation of the cation (**1a**). At this wavelength, absorptions due to the starting ethers are smaller and those due to (Tr)$^+$ and (Tr)OR are negligible. The salt (Tr)$^+$(BF$_4$)$^-$ is not sufficiently soluble in the mixed solvent used earlier to give the concentrations needed ($\geqslant 10^{-2}$M) to ensure first-order kinetic behaviour and a satisfactory absorbance change through the reactions. However, to minimise minor complications arising from decomposition of the Cr complexes in MeCN, conditions were chosen to give relatively fast reactions ($t_{\frac{1}{2}}$ < 60 s in most cases). Reactions of (Tr)$^+$ with (MG)OR (**4a,b**) were also studied in MeCN.

For each reaction studied, at least seven concentrations of cation salt were used. All reactions went to completion and good first-order kinetics over at least three half-lives were observed. Independent experiments showed that no reaction occurred in the absence of carbocation salt. Plots of the observed first-order rate constants k_ψ against [cation] were linear, passing through the origin, and the second-order rate constants k_2 (Table 1) were evaluated from the slopes; under the experimental conditions, $k_\psi = k_2$[cation].

Table 1. Rate constants for alkoxide-transfer reactions[a]

Cation	Ether	Solvent[b]	k_2/l mol^{-1} s^{-1}	$k_2^{\text{rel.}}$
Tr$^+$	(MG)OMe	MeNO$_2$–MeCOEt	3.9×10^{-1}	110.0
(**1a**)	(MG)OMe	MeNO$_2$–MeCOEt	3.5×10^{-3}	1.0
(**1b**)	(MG)OMe	MeNO$_2$–MeCOEt	3.6×10^{-2}	10.0
(**1c**)	(MG)OMe	MeNO$_2$–MeCOEt	2.0×10^{-2}	6.0
Tr$^+$	(**2a**)	MeCN	9.7×10^{-1}	5.1
Tr$^+$	(**2b**)	MeCN	5.8×10^{-1}	3.1
Tr$^+$	(**2c**)	MeCN	3.1×10^{-1}	1.6
Tr$^+$	(**2d**)	MeCN	1.9×10^{-1}	1.0
Tr$^+$	(MG)OMe	MeCN	2.3×10^{-1}	3.2
Tr$^+$	(MG)OEt	MeCN	7.4×10^{-2}	1.0

[a] At 25.0 °C. [b] MeNO$_2$–MeCOEt (40 : 60 v/v).

Reversibility of reactions. Reversibility of these alkoxide transfers was demonstrated in separate reactions of (MG)$^+$Cl$^-$ in MeCN with (Tr)OMe and its (OC)$_3$Cr complex (**2a**) in very large excess (5×10^4- and 2.5×10^3-fold, respectively). In both cases, a fall in the absorbance of (MG)$^+$ at 618 nm was observed, indicating that (MG)OMe was being formed, but the reactions were extremely slow and equilibrium had still not been established after 100 h at 25.0 °C. Although rate and equilibrium constants could not be measured, the equilibrium constants for reactions (v) and (vi) are very large (> 10^4) and the constant for reaction (v) is greater than that for reaction (vi).

$$(\mathrm{Tr})^+ + (\mathrm{MG})\mathrm{OMe} \rightleftharpoons (\mathrm{Tr})\mathrm{OMe} + (\mathrm{MG})^+ \qquad \text{(v)}$$

$$(\mathbf{1a}) + (\mathrm{MG})\mathrm{OMe} \rightleftharpoons (\mathbf{2a}) + (\mathrm{MG})^+ \qquad \text{(vi)}$$

Nucleophilic-addition and Heterolysis Reactions.—Reaction of the complexed cation (**1a**) with methanol and the reverse reaction, *i.e.* acid heterolysis of the ether (**2a**), were studied [equation (vii)] in order to assess the effect of metal complexation upon direct addition of a nucleophile to the tropylium cation. Rate constants for the forward and reverse reactions of (Tr)$^+$ with methanol [equation (viii)] have already been evaluated.[5b]

$$(\mathbf{1a}) + \mathrm{MeOH} \underset{k_r^{\mathrm{H}^+}}{\overset{k_f}{\rightleftharpoons}} (\mathbf{2a}) + \mathrm{H}^+ \qquad \text{(vii)}$$

$$(\mathrm{Tr})^+ + \mathrm{MeOH} \rightleftharpoons (\mathrm{Tr})\mathrm{OMe} + \mathrm{H}^+ \qquad \text{(viii)}$$

Interconversion of the cation (**1a**) and the ether (**2a**) in methanol (solvent) can be readily followed because of the large difference in their electronic absorption spectra (Figure). The forward and reverse reactions are clean and can be driven quantitatively in the desired direction by changing the acid concentration. The *exo*-ether (**2a**) is very susceptible to acid heterolysis, behaviour contrasting with that of its *endo*-stereoisomer (**3**) which is not converted into (**1a**) even in strong aqueous acid (2M-HCl or -HClO$_4$) but instead undergoes slow decomplexation with liberation of tropylium cation.

Rate Measurements.—Rates of conversion of (**2a**) into (**1a**) were measured at 25.0 °C in methanol containing predetermined concentrations of HClO$_4$ such that the reactions went to completion. The observed first-order rate constants k_ψ varied linearly with [HClO$_4$], and the second-order rate constant $k_r^{\mathrm{H}^+}$ (Table 2) was evaluated from the slope of a plot of k_ψ against [HClO$_4$]. This plot passed through the origin,

Table 2. Rate constants for nucleophilic additions to the cations $(Tr)^+$ and (**1a**), and for acid heterolysis of the ethers (Tr)OMe and (**2a**)[a]

Reactant	Solvent[b]	Buffer	k_f[c]	$k_r^{H^+}$/l mol^{-1} s^{-1}	k_r^{HA}/l mol^{-1} s^{-1}	Ref.[d]
(**1a**)	MeOH	None	0.07			
	MeOH	Et_3N–TsOH	2.1×10^6			11
$(Tr)^+$	MeOH	None	1.5×10^2			5*b*
(**2a**)	MeOH	None		2.2×10^5		
	H_2O–MeCN	None		3.4×10^4		
	H_2O–MeCN	$NCCH_2CO_2H$		3.4×10^4	1.2×10^2	
	H_2O–MeCN	Cl_2CHCO_2H			$(1.7—2.2) \times 10^3$[e]	
(Tr)OMe	MeOH	None		2.1×10^4		5*b*

[a] At 25 °C except for reactions of $(Tr)^+$ and (Tr)OMe which were carried out at 23 ± 1 °C (ref. 5*b*). [b] H_2O–MeCN (1:1 w/w). [c] For MeOH addition, k_f/s^{-1}; for MeO^- addition (Et_3N–TsOH buffer; ref. 11), k_f/l mol^{-1} s^{-1}. [d] Unless this work. [e] Varies with buffer concentration (see text).

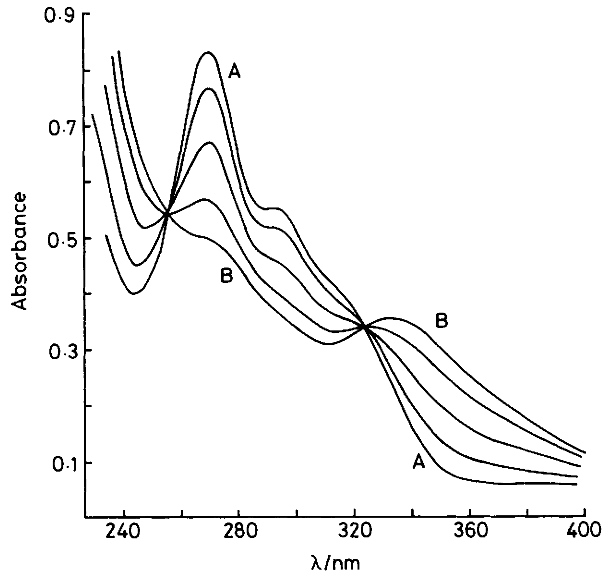


Figure. Electronic absorption spectra in methanol of the cation (**1a**) (curve A), the ether (**2a**) (curve B), and mixtures of the two obtained by adding portions (μl amounts) of $HClO_4$ (10^{-2}M) in methanol to a solution (3 ml) of (**2a**) in methanol. Isosbestic points, 256 and 324 nm; $\lambda_{max.}$ (**1a**) 270 (ε 1.02×10^4) and 290sh nm (ε 6.65×10^3); $\lambda_{max.}$ (**2a**) 270sh (ε 6.00×10^3) and 333 nm (ε 4.62×10^3)

showing that the contribution of spontaneous heterolysis to the overall rate is insignificant under these conditions and that $k_\psi = k_r^{H^+}[HClO_4]$.

Determination of the first-order rate constant k_f for spontaneous addition of methanol (solvent) to the cation (**1a**) was not straightforward. Formation of the ether (**2a**) is accompanied by generation of an equimolar amount of acid [equation (vii)] so that the contribution of the reverse reaction to the observed rate constant ($k_\psi = k_f + k_r^{H^+}[H^+]$) may become significant as the reaction proceeds, given the magnitude of k_r^{H}. In other words, it is not possible to drive the addition reaction essentially to completion unless the concentration of the organometallic substrate is kept very low. The reaction rate is also very sensitive to the presence of any basic or nucleophilic impurities (*e.g.* amines) in the methanol solvent which consume the cation (**1a**) either by direct nucleophilic addition to the ring or by general base catalysis of methanol addition (see later). A value (Table 2) for k_f was obtained for reaction at 25.0 °C of (**1a**) $(BF_4)^-$ at sufficiently low concentration in rigorously purified methanol such that essentially quantitative (> 99%) conversion into the ether (**2a**) occurred. Added salts retard the reaction, as found[9] for nucleophilic additions to other carbocations.

Table 3. pK_{R^+} Values for cation (**1a**) in methanol containing dichloroacetate buffer[a]

$10^2[Cl_2CHCO_2Na]$/M	[(**1a**)]/%	log ([(**1a**)]/[(**2a**)])	pK_{R^+}[b]
0.256	62.2	0.22	6.63
0.64	67.7	0.32	6.73
1.60	76.6	0.52	6.93
4.00	83.0	0.69	7.10

[a] At 25.0 °C; buffer ratio $[Cl_2CHCO_2Na]/[Cl_2CHCO_2H] = 1.0$; pH = 6.41 = pK_a of Cl_2CHCO_2H in methanol (ref. 5*b*); in all experiments, total [(**1a**)] + [(**2a**)] = 4.0×10^{-5}M. [b] pK_{R^+} = pH + log {[(**1a**)]/[(**2a**)]}, where %[(**1a**)] + %[(**2a**)] = 100.

The values (Table 2) of k_f and $k_r^{H^+}$ give a pK_{R^+} value of 6.5 ($K_{R^+} = k_f/k_r^{H^+}$) for the equilibrium (vii) in methanol. Direct determination of K_{R^+} was made from the relative concentrations of cation (**1a**) and ether (**2a**) in methanol (*cf.* Figure) at 25.0 °C containing dichloroacetate buffer. However, this equilibrium constant decreases with increasing [buffer] because of the salt effect which causes a decrease in k_f and an increase in $k_r^{H^+}$ with increasing $[Cl_2CHCO_2Na]$. In solutions with buffer salt concentrations up to 4×10^{-2}M, the measured pK_{R^+} value increased with increasing [salt] through the range 6.6—7.1; extrapolation of these values (Table 3) to zero [salt] gave a value close to that calculated from the rate constants.

Conversion of the ether (**2a**) into the cation (**1a**) was also followed at 25.0 °C in H_2O:MeCN (1:1 w/w). The electronic spectra of these substrates in this solvent are very similar to those in methanol (Figure). For reactions in the mixed solvent containing $HClO_4$, a plot of the first-order rate constants k_ψ against $[HClO_4]$ was linear, passing through the origin, and the $k_r^{H^+}$ value (Table 2) was evaluated as before.

Reaction with Hydroxide Ion.—The cation (**1a**) does not undergo nucleophilic addition of water in aqueous solutions of pH < *ca.* 6. Slow decomposition of the complex occurs when solutions are kept for long periods but the $(OC)_3Cr$ complex of tropyl alcohol (**2**; R = H) does not form. Reactions with aqueous solutions of high pH (NaOH, $NaHCO_3$) give[8a] a mixture of the mono- and bis-{$Cr(CO)_3$} complexes (**5**) and (**6**) of ditropyl. This reaction is accompanied by the formation, as by-products, of inorganic chromium compound(s) and tropyl alcohol, but again there is no evidence for formation of the addition product (**2**; R = H). Thus, if an aqueous alkaline solution in which the cation (**1a**) is being consumed is acidified during the course of the reaction, loss of the cation is immediately arrested but it is not regenerated.

The mechanism of formation of the ditropyl complexes has not been established, but probably involves one-electron reduction of the cation (**1a**) by a low-valent chromium species arising from partial breakdown of the complex following reaction with hydroxide ion, perhaps at the metal atom.[10b,11] Independent experiments have shown that one-electron reduction of (**1a**) can be effected by zinc metal,[8a] chromium(II) salts,[12] and carbonylmetallates,[13] the resulting 19-electron radical then dimerising spontaneously by ligand ring-coupling. We have found that the complexes (**5**) and (**6**) are also formed by reaction of the salt (**1a**) $(BF_4)^-$ with 1,8-bis(dimethylamino)naphthalene.

When the ether (**2a**) is added to water (pH *ca.* 6) or aqueous $NaHCO_3$ solutions (pH 8 ± 0.5), spontaneous and quantitative heterolysis gives the cation (**1a**). The formation of cation in these experiments is much faster than its subsequent decomposition (see earlier) which is speeded by increasing the pH of the solution in which it is generated. Similar behaviour was observed in reactions of (**2a**) with aqueous NaOH. A change of solvent from water to H_2O–MeCN (1:1 w/w) gives a *ca.* 40-fold reduction in the rate of heterolysis of the ether. A similar solvent effect was reported[9c] earlier for heterolyses of triarylmethanols and 1-ferrocenylalkanols, and the reasons were discussed.

General Acid Catalysis of Heterolysis.—Conversion of the ether (**2a**) in H_2O–MeCN (1:1 w/w) into the cation (**1a**) is general acid-catalysed in cyanoacetate and dichloroacetate buffers. The second-order rate constants k_r^{HA} for reactions catalysed by the buffer acids (Table 2) were obtained in the usual way from the increase in the observed first-order rate constants k_ψ at a fixed pH with increasing buffer acid (HA) concentration [equation (ix)]. The value of k_r^{HA} for catalysis by

$$k_\psi = k_r^{H^+}[H^+] + k_r^{HA}[HA] \qquad \text{(ix)}$$

dichloroacetic acid is not reliable because it depends on the buffer ratio and plots of k_ψ against $[Cl_2CHCO_2H]$ are linear only over a limited range of acid concentration. There is considerable reaction with hydronium ion in this buffer and it is difficult to estimate its contribution accurately.

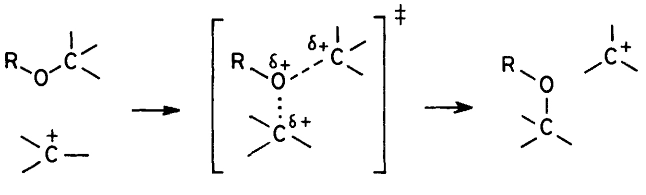
We carried out a few measurements of the rates of conversion of (**2a**) into (**1a**) in methanol containing carboxylate buffers but obtained inconsistent results. These reactions may be complicated by ion-pairing or hydrogen-bonding effects and their study was not pursued.

Discussion

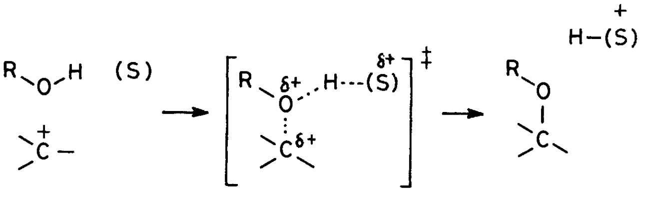
There is no doubt that π-complexation of $(Tr)^+$ with an $(OC)_3Cr$ group substantially enhances thermodynamic stability, as shown by the pK_{R^+} values for $(Tr)^+$ and (**1a**) in methanol (2.15[5b] and 6.5, respectively). The observation that the ether (**2a**) is *quantitatively* converted into the cation (**1a**) in aqueous solutions of pH *ca.* 8 shows that the pK_{R^+} value for the organometallic cation in water must be > *ca.* 9, if it is at all meaningful to cite a value for a reaction that does not exhibit reversibility; *cf.* the cation undergoing decomplexation upon reaction with hydroxide. The corresponding value[5a] for $(Tr)^+$ in water is 4.76. We have already commented[6b] that the pK_{R^+} value of 6.3 reported[14] earlier for the cation (**1a**) in water is in error.

Stereochemical and mechanistic features differentiate electrophilic reactions of $(Tr)^+$ and its metal η^7-complexes. With the latter, interaction of a ring carbon atom with a nucleophilic reagent occurs exclusively from the *exo*-face of the ring,[8b,10,11] and this bond-making is accompanied by breaking of the bond from the metal to the reacting ring carbon atom. The uncomplexed cation, of course, can react with equal ease on both faces of the ring. In comparison of rates of reaction of uncomplexed and metal-complexed cations, therefore, there is an inbuilt statistical factor favouring the former.

From the usual inverse relationship between stability and reactivity, it would be expected that metal π-complexation of $(Tr)^+$ would be accompanied by a reduction in electrophilic reactivity, and this is so. The cation (**1a**) is less reactive towards alkoxide abstraction from (MG)OMe than is $(Tr)^+$ by a factor of 110 (Table 1), and is less reactive towards addition of methanol by a factor of *ca.* 2 100 (Table 2). Different mechanisms operate for these reactions. The former involves S_E2 attack by the carbocation on the ether oxygen atom, and there is both C • • • O bond-making and bond-breaking in the transition state (Scheme 1). The transition state for alcohol addition involves C • • • O bond-making only, concerted with proton transfer to a solvent molecule (Scheme 2); see later.



Scheme 1.



Scheme 2. (S) = solvent molecule or general base

Given the difference in thermodynamic stabilities of the cations $(Tr)^+$ and (**1a**), it would be expected from the Hammond postulate that the transition state for nucleophilic addition to $(Tr)^+$ would be earlier (more carbocation-like) than that for addition to (**1a**). The difference in the magnitude of the metal-complexation effect on relative rates suggests that the extent of C • • • O bond-making in the transition state for alkoxide transfer is less advanced than in that for methanol addition. If so, loss of carbocation character in proceeding to the transition state for alkoxide transfer would be less important than for methanol addition, so that the free-energy difference between $(Tr)^+$ and (**1a**) would be less important in determining relative rates for the former reaction. We have shown earlier that there is appreciable bond-making in the transition states for addition of neutral nucleophiles to metal-complexed carbocations.[15]

Steric Effects.—Rates of alkoxide transfer from the ethers (**2a**—**d**) to $(Tr)^+$ [equation (iv)] are relatively insensitive to the steric bulk of the alkoxy group. Thus, transfer of a methoxy group from (**2a**) occurs only *ca.* 5 times faster than that for transfer of a t-butoxy group from (**2d**) under the same experimental conditions (Table 1). Likewise, rates of transfer of a methoxy group from both (MG)OMe and (**2a**) to $(Tr)^+$ are only *ca.* 2—3 times those for transfer of an ethoxy group from the corresponding ethers (MG)OEt and (**2b**). These findings suggest that the carbocation electrophile has not approached closely to the ether oxygen atom in the transition state for alkoxide transfer (Scheme 1), *i.e.* that C • • • O bond-making is not far advanced, in agreement with the conclusion reached earlier.

Solvent Effects.—Based upon very limited data, it may be concluded that the alkoxide-transfer reactions are not very

Table 4. Relative reactivities of the cations (**1a**—**c**) towards nucleophilic reactants

		Relative rate constants[a]			
Reactant	Solvent	(**1a**)	(**1b**)	(**1c**)	Ref.
Bu_3P	Me_2CO	4.4	1.9	1.0	16
Acetylacetone	$(CH_2Cl)_2$	1.0	1.9	2.3	14
(MG)OMe	$MeNO_2$–MeCOEt	1.0	10.0	6.0	*b*
MeO^- [c]	MeOH	50.0	9.8	1.0	11

[a] From second-order rate constants for *exo*-addition to the complexed tropylium ring. [b] This work. [c] Addition of MeO^- to the tropylium ring is preceded by reversible addition to the metal atom or a carbonyl ligand (refs. 10, 11).

sensitive to change of solvent. The rates of reaction of $(Tr)^+$ with (MG)OMe in $MeNO_2$–MeCOEt (40:60 v/v) and in MeCN differ by a factor less than two (Table 1), with reaction in the latter solvent slightly slower.

Heterolysis of the ether (**2a**) in water is retarded by addition of MeCN. This should make the solvent less basic by decreasing hydration of the proton (*i.e.* protonation by the solvated proton will be increased), but will stabilise the ether (*i.e.* the proton acceptor) and this latter factor is the more important.[9c]

Metal Dependence.—The dependence of the electrophilic reactivity of π-complexed hydrocarbons on the identity of the transition metal atom of a particular triad has been discussed and results tabulated.[4] Relative rate constants for reactions of the (η^7-tropylium) complexes (**1a**—**c**) with different nucleophilic substrates are in Table 4. The results show no consistent pattern but do reveal that metal-dependence effects on reactivity towards *neutral* substrates are relatively small for the metals of the chromium triad. For methoxide-transfer reactions of the cations (**1a**—**c**) with (MG)OMe, a reactivity order Mo > W > Cr was found, but the rates cover only a ten-fold change and suggest relatively small differences in activation free energies. Metal dependence of reactivity towards an anionic nucleophile (MeO^-), on the other hand, is much more marked,[11] with a reactivity order Cr > Mo > W. Further study of the relative reactivities of the cations (**1a**—**c**) towards a more extensive series of neutral and anionic nucleophiles is clearly required.

Ether Heterolysis.—Comparison of the second-order rate constants $k_r^{H^+}$ (Table 2) for the hydronium ion-promoted reactions of (Tr)OMe[5b] and the *exo*-ether (**2a**) in methanol shows that $(OC)_3Cr$-complexation of the former increases reactivity towards heterolysis by a factor of *ca.* 10.* A change of solvent from methanol to aqueous MeCN (1:1 w/w) modestly reduces $k_r^{H^+}$. Previous work[9c] has shown that acid heterolysis of alcohols in water is retarded by addition of MeCN (see earlier), but data on the relative rates of acid heterolysis of alcohols or ethers in methanol and aqueous solvents are lacking. The observation that the stereoisomeric *endo*-ether (**3**) is inert to acid heterolysis, even in strong aqueous protic acids, shows that heterolysis of the *exo*-ether (**2a**) is anchimerically assisted by participation of ring-metal bonding or metal non-bonding electrons, as found for ionisation reactions of related organometallic substrates.[2]

Alcohol heterolysis is general acid-catalysed in cases where a stable carbocation results,[17] and there is general base catalysis of additions of alcohol[18] and water[19] to preformed carbocations. The conversion of (**2a**) into (**1a**) in aqueous MeCN is general acid-catalysed and, although we do not obtain a reliable value of k_r^{HA} for dichloroacetic acid, catalytic constants for H_3O^+ and cyanoacetic acid suggest that the Brønsted α-value is close to unity, indicating a transition state in which proton transfer to the ether oxygen atom is far advanced. A similarly high α-value (0.90) was found[15] for general acid-catalysed heterolyses of tropyl alcohol and diferrocenylphenylmethanol in aqueous acetonitrile. It follows that the reverse reaction, *i.e.* addition of methanol to the cation (**1a**), would be subject to general base catalysis (Scheme 2).

Relative Nucleophilicities of Methoxide Ion and Methanol.—The mechanism of reactions of methoxide ion with the cations (**1a**—**c**) has been studied by Brown[10] and Powell[11] and their co-workers. The latter group obtained evidence for a reversible fast initial reaction of (**1a**) at the metal atom or a carbonyl ligand, followed by irreversible slower *exo*-addition of the nucleophile to the tropylium ligand to give (**2a**). From experiments with buffers in methanol, a value of 2.1×10^6 l mol^{-1} s^{-1} was calculated[11] for the second-order rate constant k^{MeO^-} for addition of methoxide ion to (**1a**) in methanol at 25.0 °C. We had already pointed out[6b] that an earlier estimate[14] (*ca.* 10^2 l mol^{-1} s^{-1}) of this rate constant is in error. The rate constants for nucleophilic additions of methoxide ion and methanol to the cation (**1a**) give $\log (k^{MeO^-}/k^{MeOH})$ *ca.* 7.5. This log ratio is of the magnitude expected from the difference in the relative nucleophilicity constants N_+ for methoxide ion (7.5) and methanol (0.5).[5c]

Experimental

General Remarks.—All syntheses of organometallic compounds were carried out under an atmosphere of dry, oxygen-free nitrogen. M.p.s are uncorrected. Microanalyses were performed by Butterworths Microanalytical Laboratory. Acetonitrile was purified as described previously.[9c] Methanol was rigorously purified by stirring over Dowex-50-X-8 acid-exchange resin, followed by distillation, redistillation from magnesium methoxide (from reaction with Mg), passage through a column of acid-washed alumina, and final re-distillation. Other solvents and reagents were purified by distillation or recrystallisation, as appropriate. Buffer solutions were prepared by partial neutralisation of aqueous solutions of component reagents in the appropriate solvent with standardised HCl or NaOH solutions. In H_2O–MeCN (1:1 w/w), the pK_a values for cyanoacetic and dichloroacetic acids are 3.80 and 2.77, respectively.[17]

Electronic spectra were recorded on Pye–Unicam SP1700 and Perkin-Elmer 402 instruments and ^1H n.m.r. spectra on Perkin-Elmer R12A and R32 instruments. Kinetic experiments were conducted with Gilford, Pye-Unicam SP8-150, and Hewlett–Packard 8 451 diode array spectrophotometers and, for stopped-flow determinations, a Durrum–Gibson instrument.

Preparation of Substrates.—The salts $(Tr)^+(BF_4)^-$,[20] (**1a**) $(BF_4)^-$,[8b] (**1b**) $(BF_4)^-$,[21] and (**1c**) $(BF_4)^-$,[21] and the complexes (**2a**)[8b] and (**3**)[8c] were prepared as described in the literature.

Tricarbonyl(η*-7-exo-ethoxycycloheptatriene*)*chromium* (**2b**). This compound was prepared by a similar procedure as described for (**2a**)[8b] by the reaction of (**1a**) $(BF_4)^-$ with NaOEt in ethanol, and was obtained in 72% yield as red crystals, m.p. 59—60 °C; $\delta(CS_2)$ 1.1 (3 H, t, Me), 3.1 (2 H, q, OCH_2), 3.6—4.4, 4.7—5.3, and 5.6—5.9 (3 H, 2 H, and 2 H, respectively, 3 m, ring protons) (Found: C, 52.3; H, 4.6. $C_{12}H_{12}CrO_4$ requires C, 52.9; H, 4.4%).

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* An incorrect value of 20 was given earlier.[6b]

Tricarbonyl(η-7-*exo-isopropoxycycloheptatriene*)*chromium* (**2c**). This compound was prepared by a similar procedure as described for (**2a**)[8b] by the reaction of (**1a**) $(BF_4)^-$ with $NaOPr^i$ in propan-2-ol, and was obtained in 65% yield as orange-red crystals, m.p. 56—58 °C; $\delta(CS_2)$ 0.9 (6 H, d, Me_2), 3.3—4.5, 4.7—5.3, and 5.65—5.9 (4 H, 2 H, and 2 H, respectively, 3 m, OCH and ring protons) (Found: C, 54.5; H, 5.1. $C_{13}H_{14}CrO_4$ requires C, 54.5; H, 4.9%).

Tricarbonyl(η-7-*exo-t-butoxycycloheptatriene*)*chromium* (**2d**). This compound was prepared by a similar procedure as described for (**2a**)[8b] by the reaction of (**1a**) $(BF_4)^-$ with $NaOBu^t$ in t-butyl alcohol, and was obtained in 56% yield as a red solid, m.p. 142—144 °C; $\delta(CS_2)$ 0.9 (9 H, s, Me_3), 3.5—4.3, 4.5—5.3, and 5.5—5.85 (3 H, 2 H, and 2 H, respectively, 3 m, ring protons). This compound decomposed on storage and satisfactory analytical data were not obtained. Freshly purified samples were used for later experiments.

Bis-(p-N,N-*dimethylaminophenyl*)*phenylmethyl methyl ether* (**4a**). All glassware and apparatus used in this preparation were washed with an aqueous alkaline solution and dried. A sufficient volume of a solution of NaOMe (*ca.* 2M) in methanol was added to a solution of Malachite Green oxalate (2.0 g, 2.2 mmol) in methanol (30 ml) to destroy the green colour of the cation. The solution was then diluted with aqueous NaOH solution (200 ml) and extracted with chloroform (3 × 50 ml). The extract was washed three times with alkaline water, dried (Na_2CO_3), and evaporated. The residual dark grey solid residue was crystallised from light petroleum–chloroform as a fluffy solid, m.p. 145—147 °C; the yield was 0.60 g (80%); $\delta(CDCl_3)$ 2.90 (12 H, s, NMe_2), 3.05 (3 H, s, OMe), and 6.6—7.7 (13 H, m, aryl protons) (Found: C, 79.5; H, 8.1; N, 8.7. $C_{24}H_{28}N_2O$ requires C, 80.0; H, 7.8; N, 8.8%).

Bis-(p-N,N-*dimethylaminophenyl*)*phenylmethyl ethyl ether* (**4b**). This compound was prepared in the same way as for (**4a**) by the reaction of Malachite Green oxalate with NaOEt in ethanol, and was obtained in 77% yield as a fluffy solid, m.p. 160—162 °C; $\delta(CDCl_3)$ 1.20 (3 H, t, Me), 2.90 (12 H, s, NMe_2), 3.14 (2 H, q, OCH_2), and 6.5—7.7 (13 H, m, aryl protons) (Found: C, 79.8; H, 8.2; N, 7.6. $C_{25}H_{30}N_2O$ requires C, 80.2; H, 8.1; N, 7.5%).

Rate Measurements.—For general remarks concerning rate measurements, see refs. 9*b*,*c* and 15. All substrates were purified directly before use, and particular care was taken to ensure that samples of $(BF_4)^-$ salts of the cations (**1a—c**) and $(Tr)^+$ were acid-free. Reactions were followed spectrophotometrically at 25.0 °C by monitoring changes in the u.v.–visible absorbance at a suitable wavelength (see text) through at least three half-lives. At least two separate determinations of each rate constant were carried out to ensure reproducibility of results. The pH of the buffer solutions used was checked by direct measurement; good agreement with calculated values was observed. Reactions with half-lives > *ca.* 3 s were followed by addition of a portion (a few μl) of a solution of the substrate to *ca.* 3 ml of the reactant solution in a thermostatted 1 cm cell. The faster reactions were followed by the stopped-flow method previously described.[9b]

Conditions were chosen to ensure that all reactions were first-order and the first-order rate constants (k_ψ) were calculated using a least-squares best-fit computer program; correlation coefficients were at least 0.999. Tables of k_ψ values from individual reactions are available as a Supplementary Publication. Derived rate constants were obtained as indicated in the text and are in Tables 1 and 2.

Addition of Methanol to the Cation (**1a**).—The conversion of (**1a**) into (**2a**) was followed at 25.0 °C by monitoring changes in absorbance at 270 and 250 nm (see Figure) resulting when a solution (a few μl) of (**1a**) $(BF_4)^-$ (5×10^{-2}M) in MeCN was added to rigorously purified methanol (3 ml). The concentration of organometallic substrate in the reaction solution was kept sufficiently low to ensure that the reaction went essentially to completion, *i.e.* so that the concentration of (**1a**) in the final (equilibrium) solution was negligible. Values of the observed first-order rate constant k_ψ increase with increasing [substrate] because of the contribution of the reverse reaction [equation (x)]. Addition of methanol to (**1a**) is retarded in the

$$k_\psi = k_f + k_r^{H^+}[H^+] = k_f\{1 + ([(\mathbf{1a})]/[(\mathbf{2a})])_{\text{equil.}}\} \quad \text{(x)}$$
$$\text{where } ([(\mathbf{1a})]/[(\mathbf{2a})])_{\text{equil.}} = [H^+]/K_{R^+}$$

presence of added salts. The effect increases through the series: salt = NaOTs < $NaClO_4$ < NaO_2CCF_3, and levels off at salt concentrations > *ca.* 0.2M where the first-order rate constant for addition is reduced about four-fold from that in the absence of salt.

Equilibrium Measurements.—The pK_{R^+} values for equilibrium (vii) in solutions of various ionic strengths were obtained from the relative concentrations of (**1a**) and (**2a**) calculated from the measured absorbances at 350 nm of solutions resulting from addition of a portion (6 μl) of a solution (2×10^{-2}M) of the ether (**2a**) in methanol to dichloroacetate buffer (exactly 3 ml) in methanol at 25.0 °C. These buffer solutions do not absorb at 350 nm. The absorbances of solutions containing 100% (**1a**) and 100% (**2a**) were measured for methanol solutions containing 10^{-3}M-$HClO_4$ and -NaOMe, respectively. Relative concentrations of cation and ether in the equilibrium mixtures were calculated from these absorbances and those of the solutions containing buffer, from the Beer–Lambert law. The pK_{R^+} values (Table 3) were calculated from relationship (xi). Similar results

$$pK_{R^+} = pH + \log([(\mathbf{1a})]/[(\mathbf{2a})])_{\text{equil.}} \quad \text{(xi)}$$

were obtained from experiments where the salt (**1a**) $(BF_4)^-$, dissolved in MeCN, was used as starting material in place of the ether (**2a**).

Reactions of (**1a**) *and* (**2a**) *in Aqueous Solutions*.—The following reactions were followed spectrophotometrically at 25.0 °C by monitoring change in absorption at 270 nm, $\lambda_{max.}$ for the cation (**1a**); see Figure.

(a) A portion (6 μl) of a solution of the salt (**1a**) $(BF_4)^-$ (5×10^{-2}M) in MeCN was added to a 1 cm cuvette containing distilled water (3 ml; pH *ca.* 6); no reaction was observed. The procedure was repeated with additions to solutions in water of $NaHCO_3$ at concentrations 10^{-3}M (pH 7.8), 10^{-1}M (pH 8.4), and 0.48M (pH 10.0). In each case, the absorbance at 270 nm fell, the rate of loss increasing with increasing [$NaHCO_3$]. Acidification (addition of one drop of 1.0M-HCl) of the solution during the course of the reaction with 10^{-3}M-$NaHCO_3$ solution immediately arrested loss of (**1a**) but did not regenerate this cation.

(b) Addition of a portion (6 μl) of a solution of NaOH (0.10M) in water to a solution of the salt (**1a**) $(BF_4)^-$ (10^{-4}M) in water caused consumption of the cation (**1a**) which could be arrested by acidification of the solution as in the previous experiment. No difference in behaviour was found when the reaction was repeated with CO_2- and O_2-free water as solvent.

(c) Addition of a portion (6 μl) of a solution of the ether (**2a**) (1.5×10^{-2}M) in methanol to water (3 ml; pH *ca.* 6) caused quantitative formation of the cation (**1a**). The reaction was first-order with a rate constant k_ψ 7.5×10^{-2} s^{-1}. When the reaction was repeated in H_2O–MeCN (1:1 w/w), formation of the cation (**1a**) was much slower (k_ψ 1.9×10^{-3} s^{-1}) and did not go to completion. Similar additions of a portion (6 μl) to solutions (3 ml) in water of $NaHCO_3$ at 10^{-3}M (pH 7.8) and 10^{-1}M (pH 8.4) also caused quantitative formation of the cation

(**1a**), followed by its much slower irreversible loss; *cf.* (a) above. The rates of cation formation ($t_{\frac{1}{2}}$ *ca.* 7—8 s) and subsequent loss were faster in the more concentrated hydrogencarbonate solution, more noticeably so for the latter reaction.

Formation of Ditropyl Complexes.—A solution of the salt (**1a**) $(BF_4)^-$ (1.0 g, 5.6 mmol) and 1,8-bis(dimethylamino)-naphthalene (1.21 g, 5.6 mmol) in CH_2Cl_2 (20 ml) was stirred for 0.5 h, then filtered, evaporated to low bulk, and chromatographed on deactivated neutral alumina with CH_2Cl_2 as solvent. Complete separation of the developed bands was not achieved but evaporation of selected eluant fractions gave pure samples of the complexes (**5**) and (**6**), identical with authentic samples.[8a]

Supplementary material (rate-constant data) is available as a Supplementary Publication No. 56711 (19 pp.).*

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* For details of Supplementary Publications, see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1988, Issue 1.

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