

Preliminary communication

THE RELATIVE ELECTROPHILIC REACTIVITIES OF THE TROPYLIUM CATION AND ITS Cr(CO)₃, Mo(CO)₃, AND W(CO)₃ COMPLEXES

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Summary

The relative rates of transfer of methoxide ion from Malachite Green methyl ether in MeNO₂/MeCOEt (2/3 v/v) to tropylium cation (Tr⁺), [TrCr(CO)₃]⁺, [TrMo(CO)₃]⁺, and [TrW(CO)₃]⁺ are 110/1/10/6, respectively.

The availability of ML_n complexes of polyenyl cations makes possible a study of the effect upon carbocation properties of π-complexation with the different transition metals of a particular triad. Earlier equilibrium [1] and kinetic [2] studies led to the conclusion that the stability and reactivity of [(η-Tr)M(CO)₃]⁺ (Tr = tropylium; M = Cr, Mo, and W) are relatively insensitive to the identity of the metal, in contrast to the behaviour of [(η-Cy)M(CO)₃]⁺ (Cy = cyclohexadienyl; M = Fe, Ru, and Os) for which electrophilic reactivity is metal dependent [3].

We have carried out a kinetic study of the methoxide-exchange reaction (eq. 1).



We used the BF₄⁻ salts of the tropylium cation (R⁺ = C₇H₇⁺ = Tr⁺) [4] and its metal complexes [(η-Tr)M(CO)₃]⁺ (M = Cr, Mo, and W) [5]. Reactions were carried out at 25°C in MeNO₂/MeCOEt (2/3 v/v) and independent experiments established that the individual reactants and products are stable in this medium. Various other solvents (e.g. MeCN, MeNO₂, Me₂CO) and solvent mixtures were tried but these proved unsuitable for various reasons (e.g. solubility problems, decomposition of organometallic substrates during slower reactions). Reactions

TABLE 1

RATE CONSTANTS FOR METHOXIDE-EXCHANGE REACTION (eq. 1)^a

R ⁺	10 ³ k ₂ (l mol ⁻¹ s ⁻¹)	k ₂ ^{rel.}
Tr ⁺	382.0	110
[TrCr(CO) ₃] ⁺	3.45	1
[TrMo(CO) ₃] ⁺	35.7	10
[TrW(CO) ₃] ⁺	20.9	6

^a In MeNO₂/MeCOEt (2/3 v/v) at 25°C; values are the slopes of least-squares best-fit plots of k_{ψ} against [R⁺] for nine data points; correlation coefficients were 0.999 or better.

were carried out under pseudo-first-order conditions by using a large molar excess (≥ 100 -fold) of R⁺BF₄⁻ over (MG)OMe (2×10^{-5} M), following the rate of formation of (MG)⁺ at 618 nm at which wavelength the absorption of the other substrates is negligible. For each reaction, nine different concentrations of R⁺ were used spanning a fivefold change. All reactions went to completion and good first-order kinetic behaviour over at least four half-lives was observed. Plots of the first-order rate constants (k_{ψ}) against [R⁺] were linear, passing through the origin, and the second-order rate constants (k_2) were obtained from the slopes ($k_{\psi} = k_2[R^+]$). The results are in Table 1.

Comparison of the rate constants (see k_2^{rel} values) shows that each of the metal-complexed cations is less reactive towards (MG)OMe than is Tr⁺. This may be related to a lower positive charge at the ring carbon atoms of the complexes and/or to the extra energy needed to break a metal-carbon bond accompanied by folding of the ring into an envelope conformation [6]. Also, because M(CO)₃ complexation strongly stabilises Tr⁺ [1,7], the transition states for reaction of the complexes may be later (i.e. less reactant-like) than that for Tr⁺. Given the statistical factor that reaction of Tr⁺ can occur from either side of the planar ring whereas only the *exo*-face of the ring in the complexes is open to reaction [8], the effect of complexation on reactivity is relatively small in free-energy terms, particularly for the Mo and W complexes. Complexation of Tr⁺ with Cr(CO)₃ has a much smaller effect upon reactivity towards (MG)OMe than for nucleophilic addition of MeOH (in MeOH solvent) where the uncomplexed cation is ca. 1500 times more reactive than the complex [7]. However, although both reactions lead to the same ether product, the mechanisms differ in that the former involves S_E displacement of (MG)⁺ by attack of a carbocation on (MG)OMe. Further work is needed to determine whether a stepwise or concerted mechanism operates.

The dependence of the rate of the methoxide-exchange reaction 1 upon the metal is more pronounced (Cr < W < Mo) than that found earlier for additions of nucleophiles such as acetylacetone (Cr < Mo < W) [2a] and Bu₃P (Mo \approx W < Cr) [2b]. Kinetic data on other addition reactions are needed before an assessment of the factors controlling relative reactivity and selectivity can be made.

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JOURNAL OF ORGANOMETALLIC CHEMISTRY, VOL. 247, NO. 1

AUTHOR INDEX

- | | | |
|--------------------|-------------------|------------------------|
| Arcas, A., 123 | Huche, M., C11 | Pahl, C., 39 |
| Artigao, M., 123 | Hunter, W.E., 1 | Pfisterer, H., 39 |
| Atwood, J.L., 1 | Hussong, K., C1 | Piacenti, F., 89 |
| | | Pourcelot, G., C11 |
| Bell, L.K., 39 | Jimenez, R., 123 | |
| Berlan, J., C11 | Jones, M., C5 | Rigo, P., C8 |
| Besace, Y., C11 | Jones, R.A., 1 | Royo, P., 33 |
| Bianchi, M., 89 | Jungmann, H., C1 | Rustemeyer, P., 7 |
| Bressan, M., C8 | | |
| Brint, R.P., 61 | Kitching, W., C5 | Scherer, O.J., C1 |
| Bunton, C.A., C14 | | Schubert, U., 7 |
| | | Seeberger, M.H., 1 |
| Cabeza, J.A., 105 | Lal, K., C14 | Serrano, R., 33 |
| Chicote, M.T., 123 | Lee, C.C., 71 | Spalding, T.R., 61 |
| | | Spencer, A., 117 |
| Deeney, F.A., 61 | Mackay, K.M., 21 | Stoppioni, P., 95 |
| Demchuk, K.J., 71 | Mani, F., 95 | Sutherland, R.G., 71 |
| Di Vaira, M., 95 | Matteoli, U., 89 | Usón, R., 105 |
| | Menchi, G., 89 | |
| Fischer, E.O., 7 | Moise, C., 27 | Vaira, M., Di 95 |
| Foster, S.P., 21 | Morandini, F., C8 | Vicente, J., 123 |
| Frediani, P., 89 | | |
| | Neugebauer, D., 7 | Watts, W.E., C14 |
| Gill, U.S., 71 | | |
| Guerus, I.L., 81 | O'Cuill, K., 61 | Yagupolskii, Yu.L., 81 |
| | Orama, O., 7 | |
| Herrmann, W.A., 39 | Oro, L.A., 105 | Ziegler, M.L., 39 |