

Evidence for an Associative Mechanism of Substitution in Octahedral Adducts of Tantalum(v) Halides

By RENÉ GOOD and ANDRÉ E. MERBACH*

(Institut de Chimie minérale et analytique, Université de Lausanne, 1005 Lausanne, Switzerland)

Summary An associative mechanism is postulated for Me_2Y ($\text{Y} = \text{S}, \text{Se}, \text{Te}$) exchange for $\text{TaCl}_5 \cdot \text{Me}_2\text{Y}$ in non-co-ordinating solvents on the basis of the kinetic dependence, activation energies, and steric effects; the reaction centre exerts some discrimination between different nucleophiles.

PREVIOUS reports suggest an associative mechanism for substitution in octahedral systems of Ti^{III} ,¹ V^{III} ,² Mo^{III} ,³ and Cr^{III} ,^{4,5} ions with low d -electron population are more likely to react by such a mechanism. However, an associative pathway has also been proposed for Rh^{III} ⁴ and Ga^{III} .⁶

In dichloromethane and in chloroform, the dimeric Nb^{V} and Ta^{V} halides react quantitatively with Lewis bases to

Activation energies for ligand exchange reactions for $\text{TaCl}_5 \cdot \text{Me}_2\text{Y}$ in chloroform.

	$\Delta H^*/(\text{kJ mol}^{-1})$	$\Delta S^*/(\text{J deg}^{-1} \text{mol}^{-1})$	$\Delta G^*(0^\circ\text{C})$ (kJ mol^{-1})
Me_2O	70.4 ± 1.9	18 ± 6	65.5 ± 0.4
Me_2S	25.7 ± 0.8	-91 ± 3	50.5 ± 0.2
Me_2Se	25.1 ± 1.3	-92 ± 5	49.8 ± 0.2
Me_2Te^a	24.3 ± 0.9	-92 ± 4	49.4 ± 0.2

^a In dichloromethane.

form monomeric, non-electrolyte adducts with 1:1 stoichiometry.^{7,8} Their relative stability constants can be determined by n.m.r. spectroscopy;⁹ at -60° the adducts

of TaCl_5 with dialkyl chalcogenides show the following sequence of stability: $\text{Et}_2\text{O} \ll \text{Me}_2\text{O} \sim \text{Et}_2\text{S} \ll \text{Me}_2\text{S} < \text{Me}_2\text{Se} < \text{Me}_2\text{Te}$.

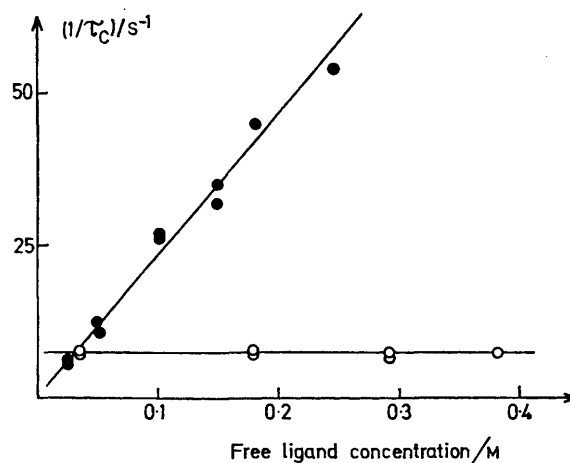


FIGURE. Ligand exchange for $0.05\text{M TaCl}_5 \cdot \text{Me}_2\text{O}$ (O) in CHCl_3 at 12° , $1/\tau_0 = d[\text{TaCl}_5 \cdot \text{Me}_2\text{O}]/[\text{TaCl}_5 \cdot \text{Me}_2\text{O}]dt = k_1$. Ligand exchange for $0.05\text{M TaCl}_5 \cdot \text{Me}_2\text{S}$ (●) in CHCl_3 at -34° , $1/\tau_c = d[\text{TaCl}_5 \cdot \text{Me}_2\text{S}]/[\text{TaCl}_5 \cdot \text{Me}_2\text{S}]/[\text{TaCl}_5 \cdot \text{Me}_2\text{S}]dt = k_2[\text{Me}_2\text{S}]$.

In the adducts of Nb^v and Ta^v chlorides studied previously the ligand exchange $MCl_5L + L^* \rightleftharpoons MCl_5L^* + L$ takes place through a dissociative mechanism D (L = RCN,¹⁰ OPCL₃¹¹). This pattern is altered for the adducts of TaCl₅ with dialkyl chalcogenides.

The kinetic dependence was examined by n.m.r. line-shape analysis. Simple equations relate the mean residence lifetime of the co-ordinated ligand, τ_c , to the first- or second-order kinetic laws¹⁰ (Figure). For TaCl₅Me₂O, the ligand exchange rate is independent of the free ligand concentration. For TaCl₅Me₂S however, the dependency is first-order; an overall second-order rate law is also observed for the adducts with Me₂Se and Me₂Te. Halide intermolecular exchange is found to be several orders of magnitude slower than ligand exchange. Niobium-93 n.m.r. spectroscopy⁸ shows that the rate of intermolecular halide exchange does not exceed the rate of ligand exchange.

The positive value of ΔS^* (Table) for TaCl₅Me₂O is consistent with a five-co-ordinated intermediate *i.e.* with a D mechanism. Conversely, the markedly negative values of ΔS^* for Me₂S, Me₂Se, and Me₂Te indicate some kind of seven-co-ordinated transition-state, and an associative substitution. Moreover, in the temperature range studied (−60 to +60 °C), the second-order rate constants increase

slightly with the basicity of the entering nucleophile. This effect is much more significant with TaBr₅, where preliminary measurements also indicated greater differences in the stabilities.

Two different mechanisms being postulated, we expected a different effect on reaction rates by introduction of a bulky oxide or sulphide. TaCl₅Et₂O shows a first-order kinetic law, with a small increase in rate, compared to TaCl₅Me₂O. The exchange of Et₂S remains second-order, but compared to Me₂S, the exchange rate is reduced by more than one order of magnitude; this implies a crowded, seven-co-ordinated transition-state.

Preliminary results show a similar mechanistic behaviour for niobium(v), but a systematic study is hindered by its easy reduction in presence of selenides and tellurides.

Considering the preceding arguments and the fact that most usual objections are ruled out by the use of non-co-ordinating solvents and the absence of charged species, we conclude that the mode of substitution for the octahedral adducts of Nb^v and Ta^v halides with soft dialkyl chalcogenides is associative.

(Received, 26th November 1973; Com. 1612.)

¹ H. Diebler, *Z. phys. Chem. NF*, 1969, **68**, 64.

² B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, 1967, **6**, 1948; W. Kruse and D. Thusius, *Inorg. Chem.*, 1968, **7**, 464; R. C. Patel and H. Diebler, *Ber. Bunsengesellschaft Phys. Chem.*, 1972, **76**, 1035.

³ Y. Sasaki and A. G. Sykes, *J.C.S. Chem. Comm.*, 1973, 767.

⁴ T. W. Swaddle and D. R. Stranks, *J. Amer. Chem. Soc.*, 1972, **94**, 8357.

⁵ D. Thusius, *Inorg. Chem.*, 1971, **10**, 1106.

⁶ D. Fiat and R. E. Connick, *J. Amer. Chem. Soc.*, 1968, **90**, 608; J. Miceli and J. Stuehr, *ibid.*, p. 6967.

⁷ K. Feenan and G. W. A. Fowles, *J. Chem. Soc.*, 1964, 2842; D. L. Kepert and R. S. Nyholm, *J. Chem. Soc.*, 1965, 2871.

⁸ R. G. Kidd and H. G. Spinney, *Inorg. Chem.*, 1973, **12**, 1967.

⁹ A. Merbach and J. C. Bünzli, *Helv. Chim. Acta*, 1971, **54**, 2536.

¹⁰ A. Merbach and J. C. Bünzli, *Helv. Chim. Acta*, 1972, **55**, 1903.

¹¹ J. C. Bünzli and A. Merbach, *Helv. Chim. Acta*, 1972, **55**, 2867.