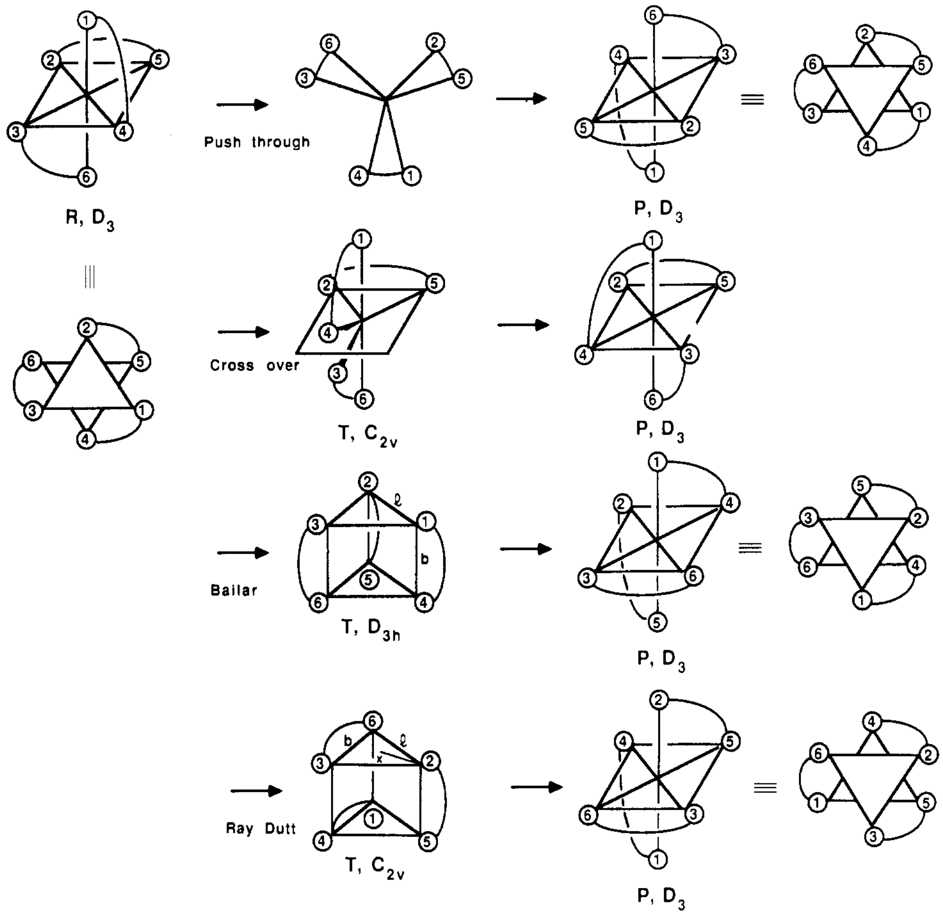

**Figure 1.** Concerted rearrangement mechanisms for tris chelate complexes.

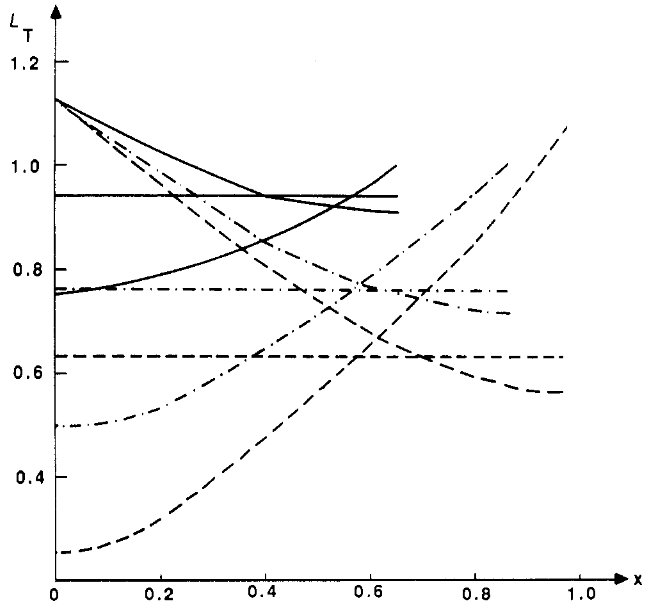

**Figure 2.** Plots of M-L bond lengths in transition states, $L_T$, for tris chelate isomerizations: (---) $b/l = 0.5$; (-·-) $b/l = 1.0$; (—) $b/l = 1.5$. Units are defined so that $l = 1$. Straight lines are the Bailar T bond lengths; curved lines are the Ray-Dutt T bond lengths.

either mechanism as there will be little difference between the energies of the two structures. In fact, for $b = 0.914l$ the M-L bond lengths of $T_B$ and $T_{RD}$ are all identical.

We have ignored dispersion energy differences in the above discussion. Where there are clear differences in M-L bond lengths, the dispersion effects are small compared with bond length energy differences. Where the bond lengths are closer in magnitude, the dispersion effects are opposite in direction from the bond length effects and so add to the competitiveness of the two mechanisms.

In conclusion, if one wishes to identify a tris chelate complex rearranging via a Bailar twist mechanism, one must have the chelate bite, *b*, much smaller than the L-L hard-sphere distance, *l* (compounds in Table II of ref 8 with $b > 2^{1/2}$ satisfy this criterion). If the converse holds, one would expect to observe only the Ray-Dutt twist, and if a compound is between these two limits, then both mechanisms will be operative.

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# Mechanistic Study of Titanate-Catalyzed Transesterification: Influence of Aggregation on Reactivity

*Sir:*

Titanium(IV) alkoxides, or titanates, have been employed as catalysts in numerous industrial processes including condensation polymerization, polymer functionalization, and monomer synthesis, but the fundamental chemistry of these reactions has remained relatively unexplored.[1] The recent contributions of Seebach, who

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(1) (a) Uri, A.; Tuulmets, A. *Org. React.* (*Tartu*) **1983**, *20*, 578. (b) *Ibid.* **1983**, *20*, 444. (c) *Ibid.* **1983**, *20*, 122. (d) *Ibid.* **1981**, *18*, 179. (e) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; p 208.

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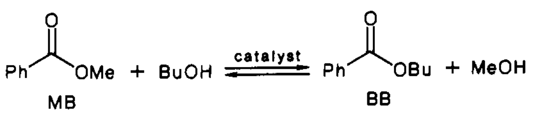
has used titanates for both catalytic and stoichiometric organic transformations,[2] including the synthesis of methyl esters by transesterification, and Sharpless, who discovered and developed titanate-catalyzed asymmetric epoxidations,[3] have renewed interest in the fundamental chemistry of titanium(IV) alkoxides. We are investigating transesterification catalysis in order to understand the fundamental reactions of titanates and to explain the notable differences that ligand structure has on their catalytic activity. Our preliminary results are reported herein.

Tetra-*n*-butyl titanate ($Ti(OBu)_4$, TBT) catalyzes the reaction of methyl benzoate (MB) with 1-butanol to yield *n*-butyl benzoate (BB) and methanol:



(1)

The reaction was studied over a TBT range of 0.5–10 mol % based on methyl benzoate (0.10 M) at 60, 80, and 100 °C, generally in butanol solvent. The reaction is first order in MB and zero order in BuOH. At low titanate levels ($1 \times 10^{-4}$ to $1 \times 10^{-3}$ M) the reaction is approximately first order in titanate, whereas at higher concentrations the titanate order is fractional, indicating a concentration-dependent change of catalyst activity. The overall TBT order is fractional and changes with temperature.

There is no observed dependence of reaction rate on alcohol concentration: initial transesterification rates for 0, 0.10, and 1 equiv of alcohol/titanate ([MB] = 0.10 M, [TBT] = 0.10 M, toluene solvent) were the same within experimental error. Experiments carried out through 3 half-lives with a large excess (10–30 equiv) of alcohol proceeded at essentially the same rate. This suggests that transesterification catalysis takes place in the coordination sphere of the metal and the only role of alcohol is to regenerate TBT by alcoholysis of methoxylated species (Scheme I). Low-temperature $^{13}C$ NMR spectroscopy[4] shows that butanol exchange with TBT is too fast to contribute to the observed transesterification kinetics. Preliminary results from magnetization transfer experiments with 1 or 2 equiv of BuOH give $k$ for alcohol exchange of $\sim 10^2$ $M^{-1}$ $s^{-1}$ at −90 °C, and the exchange is probably much faster at the elevated temperatures of the transesterification reactions.

That the catalyst order is fractional and changes with temperature suggests either of the two following points.

1. There are two or more competing pathways for catalysis that are both dependent on titanium. For example, acid or base formed by titanate hydrolysis might catalyze transesterification. Temperature changes could affect the relative rates of competing reactions.

2. The TBT is present in active and nonactive forms that are in equilibrium, probably via aggregation (Scheme I). If aggregation involves a monomer/dimer equilibrium, for example, changing temperature could affect the relative ratios and thereby change the concentration of active catalyst. Titanates are well-known to aggregate in solution; zirconates have been reported to be aggregated even at elevated temperatures in alcohol.[5]

There is no evidence that competing acid- or base-catalyzed reactions are taking place. Reactions at 80 °C in the presence of KO-*t*-Bu (1 and 10 mol % based on [TBT]) show no rate change. Under similar conditions, addition of trifluoromethanesulfonic acid results in a slight rate decrease (1.00:0.89:0.44 ratio of rates for 0, 0.10, and 1.00 mol equiv of acid based on titanium). It therefore seems likely that acidic hydrolysis products do not contribute to the observed kinetics.

Alternately, the fractional order dependence on catalyst could be due to an equilibrium between monomer and aggregated titanates. A mechanistic model including a monomer/dimer equilibrium where dimer is inactive and monomer catalyzes transesterification (Scheme I),[6] fits the observed catalyst dependence. $\Delta G$ for the equilibrium, determined over 60–100 °C from a plot of $\ln K_{ag}$ versus $1/T$, is small and negative, $-3.5 \pm 0.4$ kcal/mol, showing preference for dimer formation. $K_{ag}$, the equilibrium constant for titanate aggregation, is determined as in ref 7. At 80 °C, $K_{ag} = 149 \pm 20$, and the inactive dimer makes up 57% of the titanium when [TBT] = $1 \times 10^{-2}$ M and only 3% when [TBT] = $1 \times 10^{-4}$ M. The dimer may be inactive because its fifth and sixth coordination sites are taken up by bridging alkoxides, resulting in fewer coordination sites for ester binding and lower Lewis acidity. Alkoxide bridging between the titanium atoms of TBT to form dimers and larger aggregates has been observed by low-temperature $^{13}C$ NMR spectra of TBT containing a large excess of alcohol.[4]

We have determined activation parameters for the transesterification from data between 60 and 115 °C, where [TBT] = 0.001 M (Table I). The titanate monomer concentration was calculated from $K_{ag}$ at each temperature. Modeling the data[6] leads to specific estimates for $k_3$ and provides the following activation parameters for this step. $\Delta H^{\ddagger} = 10.4 \pm 0.7$ kcal/mol, $\Delta S^{\ddagger} = -35.6 \pm 2.0$ eu, and $\Delta G^{\ddagger} = 22.9 \pm 0.1$ kcal/mol at 80 °C. The negative $\Delta S^{\ddagger}$ is consistent with ester complexing and intramolecular reorganization (such as transfer of alkoxide to ester within the coordination sphere of the titanium) being important in the transition state.[8]

Stoichiometric reactions of meta-substituted benzoate esters with a large excess of *sec*-butyl titanate[1] have been examined. The fact that this reaction proceeds is consistent with our observation that the titanate-catalyzed transesterification is independent of alcohol concentration. The more rigorous steric requirements of the *sec*-butyl versus the *n*-butyl titanate may explain the more negative activation entropy ($\Delta S^{\ddagger} = -42$ eu) observed with *sec*-butyl titanate. Mention of zero-order alcohol dependence has been made in relation to the polytransesterification of dimethyl terephthalate with butanediol, but no experimental details were given.[9] The direct esterification of octadecanoic acid with octadecanol, catalyzed by TBT, was recently studied by Leverd, Fradet, and Marechal.[10] The activation parameters for this process indicate a very different mechanism from the transesterification, with $\Delta S^{\ddagger} = 44.4$ eu, suggesting that ester is split out from a titanium carboxylate in the rate-determining step, leaving an oxo- or hydroxotitanate behind.

The mechanism of transesterification catalysis by other metals is still unresolved, but preliminary work shows that the mechanism varies, primarily in alcohol dependence, as a function of metal catalyst. Transesterification catalysis with $ROCu(PPh_3)_2$ in benzene has been proposed to proceed via a copper-assisted nucleophilic "replacement" reaction that is alcohol dependent and linearly dependent on catalyst.[11] Divalent metal ions are also

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(2) See, for example: (a) Weidmann, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31. (b) Seebach, D.; et al. *Synthesis* **1982**, *123*. (c) Weidmann, B.; Seebach, D. *Helv. Chim. Acta* **1980**, *63*, 2451. (d) Zuger, M. F.; Schnurrenberger, P.; Seebach, D. *Helv. Chim. Acta* **1982**, *65*, 1197.

(3) See, for example: (a) Pederson, S. F.; Dewan, J. C.; Eckman, R. R.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 1279. (b) Finn, M. G.; Sharpless, K. B. *Asymmetric Synth.* **1985**, *5*, 247. (c) Schweiter, M. J.; Sharpless, K. B. *Tetrahedron Lett.* **1985**, *26*, 2543. (d) Williams, I. D.; Pederson, S. F.; Sharpless, K. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 6430.

(4) Roe, D. C.; Marsi, M., unpublished results.

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(6) (a) Stabler, R. N.; Chesick, J. *Int. J. Chem. Kinet.* **1978**, *10*, 461. (b) McKinney, R. J.; Weigert, F. J. *Quantum Chemistry Program Exchange*; Program No. 522. (c) Weigert, F. J. *Comput. Chem.*, in press.

(7) $K_{ag}$ was determined from the relationship $[Ti] = 2K_{ag}[TBT]^2 + [TBT]$, where [Ti] = total added titanium. Since at low [Ti], rate dependence is first order in titanate, $k_3$ can be obtained from $k_{obsd} = k_3[Ti]$. From this relationship, [TBT] (monomer) is calculated throughout the concentration range from $[TBT_2] = K_{ag}[TBT]^2$, where $TBT_2$ is dimer. Then $[Ti] = 2[TBT_2] + [TBT]$ becomes $[Ti] = 2K_{ag}[TBT]^2 + [TBT]$. A quadratic fit to this equation gives $K_{ag} = 149 \pm 20$ at 80 °C.

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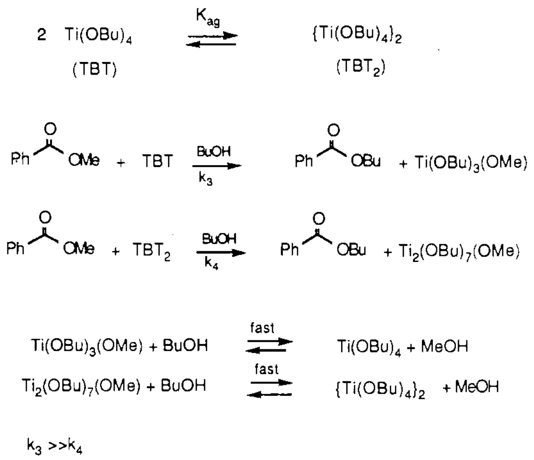
(9) Andorova, I. V.; et al. *Plast. Massy* **1987**, *7*, 41.

(10) (a) Leverd, F.; Fradet, A.; Marechal, E. *Eur. Polym. J.* **1987**, *23*, 695. (b) *Ibid.* **1987**, *23*, 699. (c) *Ibid.* **1987**, *23*, 705.

**Scheme I.** Proposed Mechanism of Transesterification[a]



[a] Reaction is fractional order in titanate catalyst and independent of alcohol concentration.

**Table I.** Temperature and Rate Data for Titanate-Monomer-Catalyzed Transesterification of Methyl Benzoate to Butyl Benzoate

| temp, K (±0.5 K) | $10^{-2}k_3$, L mol$^{-1}$ s$^{-1}$ | temp, K (±0.5 K) | $10^{-2}k_3$, L mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| 333 | 1.72 ± 0.16 | 373 | 13.00 ± 1.27 |
| 353 | 4.72 ± 0.37 | 388 | 16.88 ± 1.40 |

thought to act as Lewis acids in polytransesterification reactions;[12] for example, $Ca^{2+}$ catalysis of condensation polymerization of dimethyl terephthalate with ethylene glycol is first order in glycol, ester, and catalyst. Antimony oxide is believed to catalyze polytransesterification by ligand exchange within the antimony coordination sphere.[13]

In conclusion, we have examined some basic mechanistic features of the Ti(IV)-catalyzed transesterification and have found that, unlike some other transesterification reactions, the titanate-catalyzed process is independent of alcohol concentration. Catalyst structure is important: catalysts that maintain minimum aggregation throughout the reaction while still providing adequate coordination sites for the transesterification seem to be most active. Comparison of our results to those of Uri and Tuulmets[1] suggests that ligand structure plays an important role in determining the transition state of the reaction. Further studies of ligand structure influence will not only help in understanding transesterification catalysis, but may help elucidate other titanate-catalyzed processes as well. Toward this end, we are studying the steric and electronic effects of other ligands on transesterification and are employing spectroscopic techniques to better understand the reactions which take place in the coordination sphere of the metal.

**Acknowledgment.** I thank Drs. H. E. Bryndza and P. L. Watson for many valuable discussions and M. J. Grovola for expert technical assistance.

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(14) Contribution No. 4661.

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# Polyoxomolybdate–*o*-Benzoquinone Interactions. Synthesis and Structure of a Diacetal Derivative, $[Mo_4O_{15}(OH)(C_{14}H_8)]^{3-}$, from 9,10-Phenanthrenequinone Carbonyl Insertion. Comparison to the Reaction Products with Tetrachloro-1,2-benzoquinone, the Ligand-Bridged Binuclear Complexes $[(MoO_2Cl_2)_2L]^{2-}$, L = $(C_6Cl_2O_4)^{2-}$ and $(C_2O_4)^{2-}$, Formed via Carbonyl Insertion and Chloride Transfer

*Sir:*

The structural relationship of polyoxoanions to solid oxides has prompted a number of investigations of the interactions between poly oxometalate clusters and substrate organic molecules.[1-4] Investigations of polyoxomolybdate–carbonyl interactions have demonstrated that carbonyl insertion into a Mo–O bond is a common feature of this chemistry,[5,6] resulting in a class of tetranuclear polyoxomolybdate acetal structures for which $[RCHMo_4O_{15}H]^{3-}$ provides the prototype.[5] In the course of our continuing investigations of the chemistry of polyoxomolybdates with catechol and *o*-quinone ligand types,[7,8] we have examined the reaction chemistries of 9,10-phenanthrenequinone and tetrachloro-1,2-benzoquinone with $(Bu_4N)_2[Mo_2O_7]$ and found that, although carbonyl insertion occurs in both instances, dramatically different structural types are formed as a consequence of chloride transfer in the latter case.

Reaction of 1 equiv of 9,10-phenthrenequinone with 2 equiv of $(Bu_4N)_2[Mo_2O_7]$ in moist $CH_3OH$ followed by addition of ether results in precipitation of a yellow product that is analyzed as $(Bu_4N)_3[Mo_4O_{15}(OH)(C_{14}H_8)]$ (I)[9] after recrystallization from $CH_2Cl_2$/ether. As shown in Figure 1, (I) exhibits a tetranuclear core, related to those previously described for $[(CH_3)_2AsMo_4O_{15}H]^{2-}$,[10] $[CH_2Mo_4O_{15}H]^{3-}$, and $[HCCHMo_4O_{15}X]^{3-}$. As a consequence of both carbonyl residues inserting into the cluster core, the complex may be described as a diacetal derivative, with the $(C_{14}H_8O_4)^{4-}$ unit capping the $[Mo_4O_{11}(OH)]^{+}$ framework, providing terminal (O3 and O4) and bridging (O1 and O2) oxygen donor interactions. The most unusual features of the structure are the triply bridging hydroxy group, O16, and the single five-coordinate molybdenum center, Mo1. These features contrast with the exclusively six-coordinate molybdenum sites observed for $[CH_2Mo_4O_{15}H]^{3-}$ and $[HCCHMo_4O_{15}F]^{3-}$ and the quadruply bridging mode assumed by the hydroxyl group of $[CH_2Mo_4O_{15}H]^{3-}$.

The contrast between the chemistry of glyoxal and that of 9,10-phenanthrenequinone with $[Mo_2O_7]^{2-}$ was not anticipated. Whereas the $\alpha$-dialdehyde glyoxal initially yields the isolable formylated methylenedioxomolybdate $[OHCCHMo_4O_{15}H]^{3-}$, which undergoes intramolecular insertion of the second carbonyl

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(9) Anal. Calcd for $(Bu_4N)_3[Mo_4O_{15}(OH)(C_{14}H_8)]$, $C_{62}H_{117}N_3O_{16}Mo_4$ (I): C, 48.2; H, 7.58; N, 2.72. Found: C, 48.6; H, 7.63; N, 2.83. IR (KBr pellet, cm$^{-1}$): 2960 (s), 2875 (ms), 1490 (s), 1380 (m), 1260 (m), 1155 (m), 1070 (m), 1030 (m), 1000 (m), 920 (vs), 905 (vs), 800 (m), 755 (m), 692 (s). Crystal data: tetragonal space group $I4_1/a$, with $a$ = 48.129 (6) Å, $c$ = 13.057 (2) Å, $V$ = 30 246.2 (12) Å$^3$, $Z$ = 16, and $D_{calcd}$ = 1.35 g cm$^{-3}$. Structure solution and refinement based on 5554 reflections with $F_o \geq 6\sigma(F_o)$ (Mo K$\alpha$, $\lambda$ = 0.71073 Å) converged at a conventional discrepancy factor of 0.0545.
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