

## Gas-Phase and Solution-Phase Polymerization of Epoxides by Cr(salen) Complexes: Evidence for a Dinuclear Cationic Mechanism

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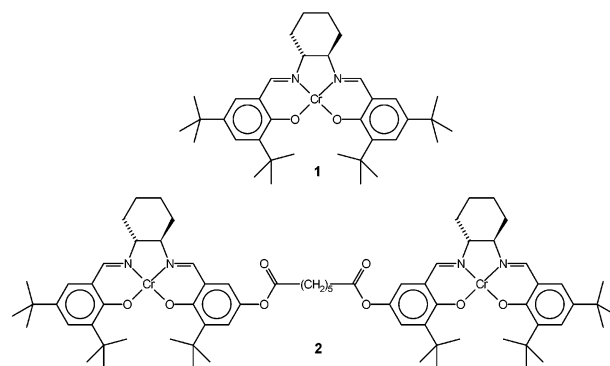
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The gas-phase reactions of a series of mass-selected mononuclear and dinuclear Cr(salen) complexes with propylene oxide suggest that the enhanced reactivity of the dinuclear complexes in gas-phase and in solution may derive from a dicationic mechanism in which the alkoxide chain is  $\mu_2$ -coordinated to two Lewis acidic metal centers. The double coordination is proposed to suppress backbiting, and hence chain-transfer in the gas-phase homopolymerization of epoxides.

The ring-opening homo- and copolymerization of epoxides is an important process for which refinements in the catalysts have produced steady improvements in the properties of the materials that can be made from inexpensive, readily available monomers. The original catalysts,<sup>1</sup> alkali metal hydroxides and alkoxides, have been superseded by transition metal alkoxides,<sup>2</sup> and, more recently, double metal cyanides.<sup>3</sup> Throughout the development of better catalysts, mechanistic studies have been hampered by aggregation of the metal complexes into clusters for which not only the kinetic order but even the stoichiometry is uncertain. We report a combined gas-phase and solution-phase study of mono- and dinuclear (salen)Cr<sup>III</sup> complexes which strongly suggests an important role for dinuclear species in the homopolymerization of epoxides. The experiment, while demonstrated for a well-defined catalyst, serves as a model for the investigation of much less well-defined systems that currently find use in production.

The catalysts were prepared by previously described methods.<sup>4</sup> Bifunctional ligands were prepared as described by Jacobsen and co-workers.<sup>4</sup> Solution-phase polymerizations

were conducted in thick-walled glass pressure tubes. Typically, neat propylene oxide (1 mL, 14.29 mmol) and Cr catalyst **2**·(Cl)<sub>2</sub> (6.2 mg, 0.0095 mmol) were incubated in a



constant-temperature bath at 75 °C (copolymerizations) or 80 °C (homopolymerizations) with stirring for 16 h (homopolymerizations) or 3 h (copolymerizations), followed by dilution with CH<sub>2</sub>Cl<sub>2</sub>, precipitation by methanol, centrifugation, and drying under vacuum. For the copolymerizations, the CO<sub>2</sub> pressure was held constant at either 13 or 25 bar. The product was checked by <sup>1</sup>H and <sup>13</sup>C NMR to confirm the identity of the polymeric product. Gas-phase studies were performed in a Finnigan MAT TSQ Quantum electrospray ionization tandem mass spectrometer as has been described previously.<sup>5</sup> Solutions of the catalyst, typically 10<sup>-5</sup> mM in methanol, were electrosprayed at 4.2 kV with a flow rate of 5  $\mu$ L/min. The heated capillary was held at 170 °C with an offset voltage of 35 V. After final desolvation in the tube lens region (tube lens potential  $\sim$  170–230 V, skimmer at ground), the desired molecular ion was selected by the first quadrupole by its *m/z* ratio. The selected ion was then introduced into the octopole collision cell with 1.5–3.5 mTorr of propylene oxide. The ion undergoes between 10<sup>3</sup> and 10<sup>4</sup> collisions with the neutral monomer in the transit time of several tens of milliseconds. The product ions are then mass-analyzed in the second quadrupole.

The first suggestion that ring-opening polymerization of epoxides involves more than one metal center was made by Vandenberg on the basis of the clean stereochemical inver-

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sion observed in the polymerization of 1,4-dichloro-2,3-epoxybutane by aluminum-containing catalysts.<sup>6</sup> Tsuruta proposed a mechanism essentially identical to Vandenberg's "flip-flop" mechanism to explain the stereoselective ring-opening of propylene oxide to largely isotactic polymer as a case of enantiomorphic site control by polynuclear metal complexes made by controlled alcoholysis of diethyl zinc.<sup>7</sup> One metal center electrophilically activates the epoxide while a second delivers the nucleophile.

Kinetic and stereochemical studies by many groups found evidence that the ring opening can be either first order or higher order in the metal ion.<sup>8–24</sup>

While there is considerable evidence for the involvement of more than one metal center at the turnover-limiting transitions state in some of the systems, the literature survey shows that the issue is far from unambiguous. Being fully cognizant of the possibility that the gas-phase and solution-phase mechanisms may diverge, we have undertaken to examine the reactions catalyzed by mono- and dinuclear (salen)Cr<sup>III</sup> complexes by electrospray ionization tandem mass spectrometry. Solution-phase polymerizations accompany the gas-phase work to establish that the systems are indeed active. While the gas-phase work suffers from a disadvantage that not all relevant species of interest may be "synthesized", it brings one very distinct advantage. The nuclearity of the

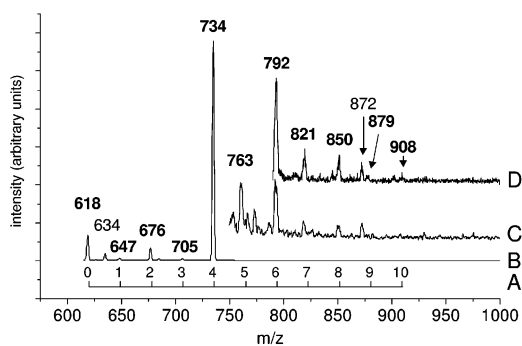
species in the reaction is predetermined in the mass spectrometric experiment, which is no inconsequential point, given the reports that even visually homogeneous solutions of zinc-alkoxide-type catalysts during propylene oxide polymerization contain substantial amounts of cluster complexes detectable by dynamic light scattering.<sup>25</sup>

In the gas-phase reaction of propylene oxide with mass-selected ions  $1^+$  and  $2^{2+}$ , with or without additional anionic or neutral ligands coordinated to the metal, the observation of an adduct mass does not necessarily imply that ring-opening of the epoxide has occurred. Simple coordination of a nucleophilic substrate, the epoxide, to an electrophilic metal center certainly takes place; ring-opening does not change the mass. However, masses for complexes corresponding to the metal complex and more propylene oxide monomer units than can be accommodated by the available coordination sites strongly suggest that oligomerization with concomitant ring-opening has in fact happened. For the species  $1^+$ , produced by electrospray of the corresponding chloride, reaction with propylene oxide yielded adduct masses with a maximum of two propylene oxide units bound to the complex. Careful examination of the baseline at higher masses failed to show any evidence of higher-order adducts. When the dinuclear complexes  $2^{2+}$ ,  $[2 \cdot \text{HOCH}_3]^{2+}$ ,  $[2 \cdot (\text{HOCH}_3)_2]^{2+}$ ,  $[2 \cdot \text{OH}]^+$ ,  $[2 \cdot \text{OCH}_3]^+$ , and  $[2 \cdot (\text{OCH}_3)(\text{HOCH}_3)]^+$  are similarly subjected to gas-phase reaction with propylene oxide, all show adduct masses, but the number of propylene oxide units varies greatly. For all ionic species, the most intense product peaks correspond to the number of propylene oxide units needed to fill all available coordination sites on the cations, for example, four for  $2^{2+}$ , and three for  $[2 \cdot \text{OH}]^+$  or  $[2 \cdot \text{OCH}_3]^+$ . The dicationic species  $2^{2+}$ ,  $[2 \cdot \text{HOCH}_3]^{2+}$ , and  $[2 \cdot (\text{HOCH}_3)_2]^{2+}$  displayed, however, long series of adduct masses reaching up to at least 10, 8, and 8 propylene oxide units for the three species, respectively. The additional adduct masses beyond the number needed to fill the available coordination sites were much weaker in intensity, but nevertheless reproducible in the mass spectrum, as seen in Figure 1. In contrast, the dinuclear, monocationic species  $[2 \cdot \text{OH}]^+$ ,  $[2 \cdot \text{OCH}_3]^+$ , and  $[2 \cdot (\text{OCH}_3)(\text{HOCH}_3)]^+$  all showed adducts containing a maximum of three polypropylene units.

The accompanying solution-phase polymerizations are listed in the Supporting Information. The turnover numbers (TONs) were computed per metal atom so that a fair comparison between mononuclear and dinuclear complexes can be made. While they do not as yet represent a complete kinetic study, it is evident from the results that the dinuclear complex displays a considerably higher TON than does its mononuclear analogue. While the appropriate gas-phase copolymerization experiments are not yet available for comparison, the same trend is evident for copolymerization of epoxides and CO<sub>2</sub>, at least at the concentrations and temperatures used in this study. Similar trends are evident for the comparable mononuclear and dinuclear Co<sup>III</sup> complexes in both homo- and copolymerizations. The gas-phase

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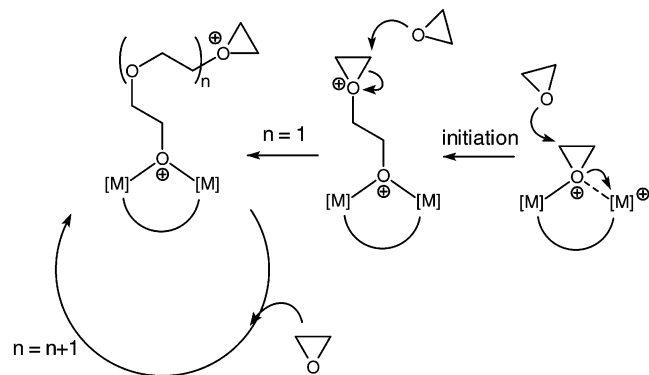


**Figure 1.** Daughter ion mass spectrum of the gas-phase reaction between mass-selected ions  $2^{2+}$  ( $m/z = 618$ ) and propylene oxide. Trace A shows a scale with the number of propylene oxide units added onto a dicationic species at  $m/z = 618$ . Trace B shows the daughter ion spectrum in which the largest species at  $m/z = 734$  contains four units of propylene oxide. Trace C shows a section of the same spectrum with a 1000-fold magnification. Trace D shows an independent measurement of the same region, indicating that the small peaks are reproducible.

observations can be summarized as follows: dinuclear complexes for which the solution-phase results show higher polymerization activity display much enhanced oligomerization activity in the gas-phase in comparison to the mononuclear complexes which show no evidence for oligomerization in the gas-phase and lower activity in solution.

The initial impulse to interpret the superior gas-phase performance of the dinuclear complexes as support for Vandenberg's flip-flop mechanism falters on closer examination of the mass spectrometric data. While both gas- and solution-phase reactions of the complexes with propylene oxide demonstrate that at least some dinuclear complexes are clearly superior in the ring-opening polymerization, it is the dicationic species  $2^{2+}$ ,  $[2 \cdot \text{HOCH}_3]^{2+}$ , and  $[2 \cdot (\text{HOCH}_3)_2]^{2+}$  that show gas-phase activity. The monocationic species  $[2 \cdot \text{OH}]^+$ ,  $[2 \cdot \text{OCH}_3]^+$ , and  $[2 \cdot (\text{OCH}_3)(\text{HOCH}_3)]^+$  are inactive. The flip-flop mechanism would have predicted just the opposite. The result suggests a cationic mechanism, Scheme 1, rather than an anionic "flip-flop" mechanism for ring-opening polymerization of propylene oxide, at least in the gas-phase. The advantage conferred by two metal centers can be rationalized by the alternative mechanism in which the metal-bound end of the growing chain is bound as a  $\mu_2$ -alkoxide; the growing end would then be a oxiranium cation which reacts with further epoxide monomer units. Given that Darensbourg showed<sup>22</sup> for the same catalyst (but mono-

#### Scheme 1



nuclear) that chain transfer was substantial, and that chain-transfer occurred through back-biting, the advantage conferred to polymer formation by a dinuclear catalyst can be ascribed, at least in part, to the suppression of backbiting by the now-sequestered  $\mu_2$ -alkoxide end of the chain. Suppression of backbiting leads then to longer oligomer chains.

Moreover, given that the other end with the oxiranium cation must be trapped by the epoxide monomer acting as a neutral nucleophile, the dinuclear complex should do better in the initiation step because  $\mu_2$ -coordination of the first epoxide unit makes it more electrophilic. The peak intensities in the gas-phase experiment in Figure 1 demonstrate that the initiation step may constitute a bottleneck, at least for the cationic polymerization mechanism. Precisely, the  $\mu_2$ -coordination mode for the initial epoxide has been shown experimentally<sup>26</sup> and computationally<sup>27</sup> to enhance markedly the ring-opening rates of that epoxide by neutral amine nucleophiles. Cationic mechanisms for epoxide ring-opening polymerizations are known,<sup>28</sup> but they have become less prominent in the literature in recent years. Darensbourg's observation,<sup>22</sup> albeit for the cyclohexene oxide/ $\text{CO}_2$  system, that the copolymerization proceeded with no stereocontrol in the ring-opening step, would also be more consistent with a cationic mechanism. The  $^{13}\text{C}$  NMR spectrum of the methine region<sup>29</sup> of the poly(propylene oxide) produced in solution by  $[2 \cdot (\text{Cl})_2]$  (see Supporting Information), the dinuclear analogue to Darensbourg's complex, showed predominantly regioregular, head-to-tail homopolymer with a more than statistical fraction of ii triads, i.e., partial stereoselectivity, indicating that the solution-phase homopolymerization may proceed differently from that in gas-phase, at least for some conditions. It would not be surprising that competition between multiple energetically close mechanisms can be tipped one way or the other by small changes in structure or conditions.

We have reported a gas-phase and solution-phase study comparing mono- and dinuclear (salen)Cr<sup>III</sup> complexes as catalysts for the ring-opening polymerization of propylene oxide. The gas-phase methods allow the selection of the specific reactive species. The mononuclear complexes show no evidence for polymerization activity in the gas-phase, whereas the dicationic dinuclear ones do. Surprisingly, the monocationic dinuclear species, which the prevalent mechanistic model would have predicted as being ideal, show no polymerization activity. This leads to the proposal of a dinuclear cationic mechanism for the reaction, at least in the gas phase.

**Supporting Information Available:** Additional data and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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