Evidence for the Polymerization of Ethylene Catalyzed by Ti^+ in the Gas Phase

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In this communication, we report the polymerization of ethylene molecules induced by an atomic ion, namely Ti^+ , in the gas phase. The experiments are performed by using a newly built selected ion drift tube with laser vaporization source apparatus operated at thermal energies. So far, up to twenty ethylene molecules are found to react with Ti^+ . The evidence that a large number of ethylene molecules react with, and become bonded onto, Ti^+ at room temperature strongly suggests that Ti^+ induces a reaction between the ethylene molecules that leads to the formation of an ethylene polymer. (*J Am Soc Mass Spectrom* 1992, 3, 464–466)

In past years the role of titanium species in the catalysis of olefin polymerization has prompted several studies of the gas-phase reactions of titanium ions species [1–4]. This has been due in part to the expectation that the studies of the gas-phase chemistry of titanium ions in the absence of a solvent or crystal environment could provide useful information leading to improved understanding of the mechanism of olefin polymerization catalyzed by the Ziegler-Natta class of catalysts [5]. Here we report that the polymerization of ethylene can also be catalyzed in the gas phase by bare Ti^+ at thermal energies.

A selected ion drift tube technique in conjunction with a laser vaporization source [6] is used in the present studies conducted at thermal energies. Ti^+ is produced by pulsed laser vaporization. To eliminate interference from other ionic species produced by the source, a quadrupole mass spectrometer is used to mass select only Ti^+ for injection into the drift tube where multiple-step reactions of the ion with ethylene molecules occur. A second quadrupole is employed to analyze the reaction product distribution. The total pressure in the reactor is about 0.7 torr with He as the buffer gas, and the experiments were conducted at room temperature.

Generally speaking, Ti^+ reacts rapidly with ethylene, and the primary reaction rate is close to the collision rate [6]. The products from the reaction are the complexes in which a number of ligands are "attached" onto Ti^+ . At very low partial pressures of

ethylene ($P_{\text{ethylene}} < 0.10$ mtorr), the products of the first four reaction steps are observed to be dominant. With an increase of the partial pressure of ethylene, the products of these initial steps are observed to undergo further reactions with ethylene molecules, whereby their signal intensities decrease dramatically, and finally disappear. Meanwhile, the signal corresponding to the products of further sequential reactions grows gradually, and eventually becomes dominant. Figure 1 is a typical mass spectrum, in the mass range from 150 u to 480 u, resulting from multiple-step reactions of Ti^+ with ethylene molecules at an ethylene partial pressure of about 0.015 torr. The peaks labeled 4 to 15 correspond to the products of the fourth to the fifteenth reaction steps. The peaks labeled by * and observable in the low mass range may result from impurities such as propylene; alternatively, they may be part of a minor competitive reaction mechanism, as mentioned below.

We have carefully examined the products from the first eight reaction steps. In general, the first four reaction steps involve both association and dehydrogenation reactions, while the association reaction or attachment of ethylene molecules is found to be the only major channel operative in the fifth to the eighth reaction steps. Details of the chemistry of the reactions will be published later [7]. Due to weak signals, a high resolution determination of each peak corresponding to the products from larger than the ninth reaction step was not possible. However, measuring the center position of each peak in the mass spectra, we find that the space between the peaks is even and corresponds to 28 u, which is the mass of one ethylene molecule. Hence, we are certain that the peaks in the higher mass range correspond to the higher order attachment of ethylene molecules onto Ti^+ .

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Figure 1. The product mass spectrum resulting from the higher order reaction steps of Ti^+ with ethylene, in the mass range from 150 to 480 u, at an ethylene partial pressure of 0.015 torr. The peaks labeled 4 to 15 correspond to the products from the fourth to the fifteenth reaction steps, respectively. The * labeled peaks may result from impurities in the ethylene gas or from the formation of bis-benzene (see footnote 1) [8].

So far, at least twenty ethylene molecules have been found to react with Ti^+ , and they bond onto Ti^+ sufficiently strongly to survive sampling and mass spectrometric detection. There are two possibilities to account for a large number of ethylene molecules being bound onto a bare Ti^+ at room temperature¹. One would involve simple association or clustering of ethylene onto Ti^+ , while another possibility is that polymerization of the reactant molecules has occurred. In other words, a large number of ethylene molecules react with each other to form a polymer molecule that bonds onto Ti^+ . However, considering the fact that the experiments are not performed at low temperature and that ethylene has no dipole moment, it is virtually impossible that as many as twenty ethylene molecules are able to associate on one bare Ti^+ . In fact, the argument was strongly supported by many test experiments made on this point in our laboratory.

We have performed studies on the reactions of other transition metal ions such as V^+ , Zr^+ , Ta^+ [8], and Ag^+ [9] to explore the possibility that a large number of molecules could cluster onto a bare metal ion at room temperature. With pure ethylene gas of

0.35 torr, the maximum number of ethylene molecules that can attach onto these ions is less than eight! Additionally, when we studied the reactions of TiO^+ with ethylene, and Ti^+ with propylene, surprisingly no higher order reaction step than the fourth was found. Only three ethylene molecules are observed to attach onto TiO^+ , and four propylene molecules onto Ti^+ . Clearly, these results indicate that the clustering reactions cannot result in the bonding of over twenty ethylene molecules onto a bare Ti^+ at room temperature.

Therefore, polymerization appears to be the only possibility to account for the fact that a large number of ethylene molecules can attach onto Ti^+ at room temperature (see footnote 1). We have developed a simple model to interpret the ethylene polymerization process induced by Ti^+ in the gas phase. The model suggests that the ethylene polymerization follows a mechanism similar to the one by which the condensed-phase olefin polymerization catalyzed by Ziegler-Natta catalyst proceeds [10]. Details of the model and other perspectives on the finding will be discussed in a full article [7].

There have been several reported observations of polymerization induced by transition metal ions in the gas phase. For example, Irikura and Beauchamp [11] found methane oligomerization induced by the third row transition metal ions. The present work provides another good example to demonstrate that gas-phase ion chemistry enables one to probe important polymerization processes that are known to occur in the condensed phase.

In summary, we have conducted an experiment to study the gas-phase multiple-step reactions of Ti^+ with ethylene at thermal energies. So far, at least twenty ethylene molecules are found to react with, and also to bond onto, the Ti^+ . These findings suggest that the proposed ethylene polymerization catalyzed by Ti^+ has occurred. That is, the ethylene molecules react with each other, induced by Ti^+ , to form an ethylene polymer which bonds directly onto Ti^+ .

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¹There has been a report that ethylene molecules can react with Nb^+ to form bis-benzene (see *Inorg. Chem.* **1989**, *28*, 3511). One may argue that such a large number of ethylene attachments onto Ti^+ can be attributed to the formation of benzene rings from ethylene reactions with Ti^+ , followed by the benzene ring coupling reactions (see *J. Am. Chem. Soc.* **1990**, *111*, 2387, and *Organometallics* **1991**, *10*, 1244). The formation of benzene from ethylene molecules and the sequential ring coupling need the loss of at least one hydrogen molecule from each of the ethylene molecules. As described in the text, it is observed in this work that beyond the fourth reaction step, ethylene attachment instead of its dehydrogenation is dominant in the further sequential reactions of Ti^+ with ethylene molecules. Therefore, the argument cannot account for the present result. However, the argument might be useful to interpret the origin of the peaks labeled *. Because the peaks are in the middle of the polymer peaks, it is also likely that these peaks could result from the multiple-step dehydrogenation reactions of ethylene molecules with Ti^+ , which lead to the formation of the bis-benzene structure, as in the case of the reactions with Nb^+ .

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