

# Recycling and Reuse Technology Transfer Center

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**Modeling the effect of an iron catalyst on the dehydrochlorination of PVC using LD-FT-ICR MS ASMS. Palm Springs, CA.**

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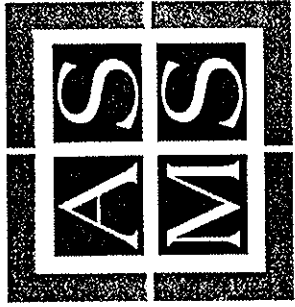
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# PROCEEDINGS



**The 45th ASMS Conference  
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## MODELING THE EFFECT OF AN IRON CATALYST ON THE DEHYDROCHLORINATION OF PVC USING LD-FT-ICR MS

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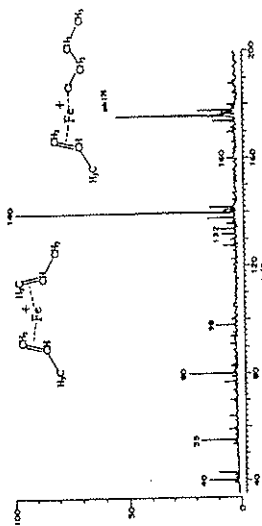
With the advent of new polymer technology, many different types of plastics and plastic additives are being produced. These new types of additives and plastics make the recycling of polymers increasingly difficult. Pyrolysis is a recycling technique that allows for the thermal degradation of polymers and the retrieval of many different hydrocarbons. Pyrolysis is utilized to thermally degrade organic compounds and retrieve economically viable products from difficult to recycle starting materials. Since pyrolysis is based on thermal decomposition, the products that are produced are dependent on the amount of thermal energy that is allowed into the system. With the difficulty in knowing what hydrocarbons are going to be produced from the different types of plastics, a cost effective way to screen polymers rapidly needs to be developed.

One relatively new and innovative way to rapidly screen the products that are produced under pyrolytic conditions is to use pulsed laser heating. Under pulsed laser heating, samples can be subjected to a very large and rapid temperature increase which simulates pyrolytic conditions. When coupled with laser desorption, FT-ICR MS allows for the study of thermodynamic and kinetic properties of the polymer under rapid heating conditions.

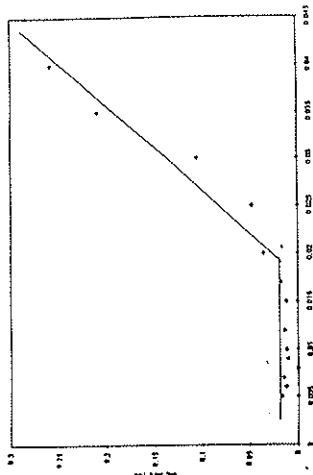
The scope of the following research centers around LD-FT-ICR MS as a tool to evaluate the thermodynamics of the dehydrohalogenation reaction during thermal degradation of poly(vinyl chloride) (PVC). Specifically, this research investigates the gas-phase reaction of metal ions with chlorinated hydrocarbons as a model of metal insertion with the poly(vinyl chloride) monomer. These gas phase reactions offer insight into the dehydrochlorination step occurring during PVC pyrolysis. This technique can also provide valuable information pertaining to the effects of an iron catalyst on the enthalpy of this reaction.

All gas-phase reactions were performed on an Ion Spec OMEGA 50 FT-ICR mass spectrometer. A stainless steel direct insertion probe was attached to the chamber for introducing a solid or involatile sample. The solid samples were ionized/desorbed by a Continuum Minilite Nd:YAG laser. The operating frequency of the laser was quadrupled to 266 nm with a pulse width of 4 nanoseconds. The repetition rate of the laser was controlled by the IonSpec OMEGA 50 interface program at a maximum rate of 10 Hz. The energy output was 20 mJ with a peak power of 0.5 MW which allows thermal degradation and ionization/desorption to occur.

The threshold energy required to cause the dehydrohalogenation reaction was studied using CID. The precursor ion was accelerated using a resonant rf electric field and allowed to collide on the residual neutrals. The amount of energy imparted to the precursor ion was varied by altering the length that the excitation field was applied. To investigate the dehydrohalogenation reaction in the gas phase, 1-chloropropane was selected to model the monomer of PVC. Iron ions were ablated and isolated in the presence of chloropropane. The iron sequentially reacted to form a  $C_3H_7Cl-Fe-C_3H_5$  complex ( $m/z$  176). The portion of this complex formed with high internal energy dissociated to form the  $(C_3H_5)_2Fe$  ( $m/z$  140).



The remaining  $C_3H_7Cl-Fe-C_3H_5$  complex ( $m/z$  176) was cooled by collision with the background neutrals and then isolated. These ions were then given varying amounts of translational energy using resonant excitation and allowed to collide into the neutrals. The internal energy generated by the CID resulted in the formation of the  $(C_3H_5)_2Fe$  complex ( $m/z$  140) by a  $\beta$ -hydrogen-halogen elimination reaction.



Using an effective electric field strength of 56.6 V/m, the duration of the excitation can be used to calculate the translational energy of the complex. From the intercept, the threshold energy required for the dehydrohalogenation reaction to occur in the gas phase in the presence of iron was determined to be 1.8 Kcal/mole or 7.6 kJ/mole. Previous research in the pyrolysis of PVC has shown that HCl gas is first evolved at 350°C or 623 K. The kinetic energy at this temperature corresponds to 3/2 RT per mole, leading to an empirical value of 7.8 kJ/mole.

The good correlation of the results obtained using LD-FT-ICR MS with those observed from pyrolysis reactors suggests that FT-ICR can be used to effectively model pyrolysis reactions. Furthermore, the observed reduction of the energy required for the dehydrohalogenation reaction in the presence of iron also suggests that iron may be a useful catalyst in the recycling of halogen containing plastics.