

Study of R-1336mzz(Z), R-1336mzz(E), and R-1233zd(E) Stereoisomerization at Elevated Temperatures

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ABSTRACT

Decarbonization efforts to reduce the use of fossil fuels for both comfort and process heating has challenged traditional vapor compression heat pump systems to be run at temperatures above traditional comfort cooling and refrigeration applications. These elevated temperatures introduce new challenges for the refrigerant and lubricant system, specifically long-term chemical stability of the working fluids. In some cases, application temperatures being proposed are at or near the traditional ASHRAE 97 highly accelerated test temperature of 175°C(347°F) for comfort applications. Because of this, new standard testing conditions using Arrhenius theory may need to be applied to select proper test temperatures to understand the long-term chemical stability and equipment reliability risks of these systems.

AHRTI (Air-Conditioning Research Technology Institute), with funding from the US Department of Energy Building Technology Office, and NYSERDA (New York State Energy Research & Development Authority) sponsored the second phase of the AHRTI Project 9016 to continue the study of Low GWP (global warming potential) refrigerants. Phase 2 of this project expanded upon the chemical stability testing with more system materials of construction and included material compatibility of common non-metallic materials used in refrigerant containing systems. This expanded testing included understanding the impact on stereoisomerization of R-1336mzz(E&Z) when subjected to highly accelerated life tests (HALT) with and without various materials. The authors tested R-1233zd(E) in conjunction with this testing through funding from their employer.

This paper summarizes stereoisomerization results of R-1336mzz(Z), R-1336mzz(E), and R-1233zd(E) tested at very highly accelerated life test (VHALT) conditions at multiple test temperatures with various catalysts.

1. INTRODUCTION

Cooling and refrigeration operation of vapor compression cycles leads to, in general, moderate temperatures experienced by the refrigerant, lubricant, and materials of construction. Evaporator temperatures are well below ambient, while condensing temperatures can be 10°C to 15°C (15°F to 25°F) above ambient, which are not major concerns from a chemical stability standpoint. Compressor discharge temperatures (CDT) and superheated refrigerant can be at much higher temperatures above ambient, however the amount of time the refrigerant or lubricant spends at these temperatures is short. Kujak and Sorenson proposed a new interpretative numerical methodology for extrapolating small scale HALT results to real life heating ventilation air conditioning and refrigeration (HVACR) based on operational conditions which utilized the time the refrigerant spent at various operational conditions (Kujak and Sorenson, 2018). They showed that the refrigerant only spends about 0.03% of one hour at CDT conditions, while the refrigerant spends most of its time at condenser temperatures and lower. The refrigerant spends about 32%, 59%, and 9% of its time, respectively, at evaporator, condenser, and compressor conditions. They demonstrated, based on air cooled operational conditions, that the typical HALT conditions of 175°C (347°F) for 14 days would equate to approximately 1200 years of air-cooled cooling operation, which is an unreasonable or unrealistic acceleration factor. They recommended that a 150°C (302°F) for 14 days would be a

more reasonable, lower temperature to consider for HALT. Their reasoning was that running very short time testing at too high of temperatures could kick off chemical reactions that normally would not occur in operating equipment. They additionally proposed that running at lower temperatures for long time periods would be a more reasonable approach as well.

Utilizing vapor compression cycles for heating operations to provide comfort heating and higher temperatures required for processes now drives a different understanding on how to conduct HALT and translate results to equipment operation and life expectancy. Figure 1 provides various heat pump temperature levels adapted from Peureux and Bobelin (Arpagaus, 2018). The refrigerant and lubricant in vapor compressor heating equipment will now see temperatures much higher above ambient conditions and previous experiences with comfort cooling or refrigeration applications will not translate well. Now in a comfort or process heating application, the refrigerant can see warm ambient conditions in the evaporator of 30°C (85°F) which were typical condenser cooling operational conditions. The condenser could see temperatures up to 80°C (176°F) for comfort heating, which challenges the chemical stability of the refrigerant with system materials. These temperatures now challenge the ability to translate short term chemistry lab HALT evaluations into the need to increase testing temperatures to much higher temperatures (Very HALT) than 175°C (347°F). VHALT temperatures of 200°C (392°F) to 230°C (446°F) seem to be appropriate for maintaining a reasonable materials screening evaluation for process heating conditions.

Unfortunately, running at these elevated temperatures can lead to new chemical reactions never observed by industry researchers and likely not to be present in heating applications. With these examples in mind, it becomes evident and crucial that the researcher understands the implications of accelerated testing in choosing appropriate test conditions to develop accelerated test models. As seen in Figure 1, VHTP heat pumps can run as high as 160°C (320°F). Using Arrhenius theory, the general understanding that a chemical reaction doubles for every 10°C (18°F), it can be realized that testing must be run at very high temperatures, run for a very long time, or both to obtain reasonable understanding of chemical stability of fluids in these systems.

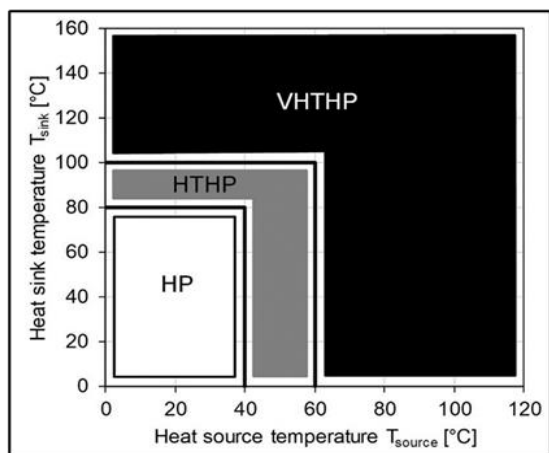


Figure 1. Proposed temperature levels for heat pumps (HP), high temperature (HTHP) and very high temperature (VHTP)



Figure 2. Possible Chemical Reactions with Haloolefins

Olefin or unsaturated (carbon-carbon double bond) refrigerant chemistry introduces the possibility for new and more complicated refrigerant system chemistry as compared to saturated refrigerants. Figure 2 summarizes the possible chemical reactions that can occur with haloolefins. Leehey and Kujak provided a comprehensive review of possible mechanistic and kinetic reactions pathways for various common hydrofluoroolefin (HFO) and hydrochlorofluoroolefins (HCFO) chemistries (Leehey and Kujak, 2023). Good refrigerant chemical stability in HVACR systems is defined as the ability to perform over a wide range of temperatures in the presence of materials (necessary for the system operation) with limited deterioration. New refrigerants must have an inherent level of thermal stability before being considered for use in HVACR systems. Once the general thermal stability of the refrigerant alone is established, it is then subjected to a wide range of construction materials and potential system

containments, like residual air, water, and manufacturing process chemicals; the refrigerant must not be adversely affected by these materials.

This study focused on understanding the stereoisomer rearrangement reactions and rates with HFO-1336mzz(Z), HFO-1336mzz(E), and HCFO-1233zd(E) with and without various typical system construction materials as catalysts including mixing the R-1336mzz isomers together to see if there are isomer concentration effects. Going forward, these refrigerants will be referred to as mzz(Z), mzz(E), and zd(E). Small rearrangements in stereochemistry may seem to be inconsequential but can result in a rather large boiling point and property difference. The R-1336mzz isomers have a boiling point difference of 26 K (47 R) and a large difference in critical temperature of 31 K (56 R). R-1233zd(E) has a boiling point of roughly 18°C (64°F) and R-1233zd(Z) has boiling point of 39°C (102°F), which is a boiling point difference of 21 K (38 R) respectively.

Formation of the alternate stereoisomer in a system designed for the other isomer in large amounts would significantly affect system performance and operation. In general, trans-alkenes are less susceptible to stereoisomer rearrangement than cis-alkenes, due to the increased steric unfavorability of the substituents in the cis-isomer. Given stereoisomers evaluated, it is expected that the trans isomers mzz(E) and zd(E) would not be susceptible to stereoisomer rearrangement to the cis isomers mzz(Z) and zd(Z). There are exceptions to this rule with fluorinated alkenes, but even if the “E” is the most stable isomer, it can still be prone to rearrangement if exposed to the right combination of catalyst and temperature. Since, in many ways, the “E” isomer is in equilibrium with the “Z” isomer, this equilibrium can be upset when given the right chemical inputs. This study was proposed to provide some initial data for these refrigerants to determine how prone they are toward stereoisomer rearrangement.

2. EXPERIMENTAL

Chemical stability evaluations were conducted via sealed glass tubes using ASHRAE Standard 97 methodologies (ASHRAE 97, 2007) for all exposures. A mixture of 50% refrigerant/50% lubricant by weight was used for conditions containing lubricant. All exposures were conducted with and without the presence of a catalyst material and/or lubricant. Table 1 provides a summary of all the catalyst details.

Three series of experiments were conducted with the R-1336mzz stereoisomers: 100% R-1336mzz(Z), 100% R-1336mzz(E), and roughly a 50/50 mixture by weight of both isomers with and without various catalysts at various temperatures for 14 days. The R-1233zd(E) experiments were conducted with 100% R-1233zd(E) with and without various lubricants and catalysts at various temperatures for 14 days. All lubricants contained an antioxidant.

Analytical assessments for all conditions included analysis of refrigerant breakdown by Gas Chromatography (GC) with a calibrated Thermal Conductivity Detector (TCD). In addition, refrigerant breakdown via anion analysis by High Pressure Liquid Chromatography (HPLC) and headspace analysis by Gas Chromatography Mass Spectroscopy (GC-MS) were also conducted to identify any unusual breakdown products. For the conditions containing lubricant, total acid number (TAN) and dissolved elements by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) were conducted. Only the refrigerant stereoisomer rearrangement results from GC-TCD analysis are reported and discussed in this paper.

Table 1: Summary of Catalyst

Catalyst	Catalyst Details
Metallic Materials	
Aluminum (Al)	UNS AL3800, cut from casting material,
Iron (Fe)	1095 Spring Steel
Copper (Cu)	110 Copper ½ Hard Temper, 99.9% Cu min
Zinc (Zn)	Zinc-Aluminum Alloy, Zamak ZA 8 Ingot
Lubricants	
Mineral Oil 1 (MO 1)	60 cst naphthenic lubricant
Mineral Oil 2 (MO 2)	100 cst naphthenic lubricant
Polyolester (POE)	220 cst lubricant
Polyolester with Additive (POE Add)	220 cst lubricant with antiwear additive

3. STEREOISOMER RESULTS

3.1 Study of R-1336mzz(Z) Stereoisomerization Rates

A total of four single metallic materials and a combination of copper/aluminum/iron catalysts used in the construction of HVACR equipment were evaluated with pure mzz(Z). The mzz(Z) did contain, as received, about 0.01% of the mzz(E) isomer. Sealed glass tubes were prepared and exposed for 14 days at 175°C (347°F), 200°C (392°F), and 225°C (437°F). Figure 3 provides a summary of the results in parts per million (ppm) of the mzz(E) isomer produced per day with and without various catalysts at the test temperatures listed above.

As expected, the mzz(E) isomer was produced at rates of 50 ppm to 800 ppm per day depending on the catalyst and temperature. Single catalysts, like iron and zinc, seemed to result in the transformation of the mzz(Z) to the mzz(E) at rates of 5 to 8 times faster than aluminum and copper. While aluminum and copper did not have an accelerating effect, the three-metal catalyst combination, which contained iron, accelerated the conversion similar to conditions where iron was tested alone.

One must remember that these are very high temperatures and the reaction rates as shown are single data points and more data points would be needed to understand the repeatability and reproducibility of these results. Generally, to understand these conversion rates further, one could use Arrhenius reaction rate theory for these experiments. Assuming a 150°C (302°F) process heating vapor compression outlet temperature for a full year operation, the 175°C (347°F) is about 6-fold acceleration, the 200°C (392°F) is about a 32-fold acceleration, and 225°C (427°F) is about a 72-fold acceleration for the 14-day exposure. If you assume 10 years of 24/7 unit operation (87,650 hours), sealed tubes will need to run for approximately 600 days ((87650 hours of operation/24 hour/day)/6 times acceleration factor)), 115 days, and 50 days, respectively, to fully understand the stereoisomerization impacts. Based on just the iron catalyst data forming about 800 ppm of the mzz(E) per day at 225°C (427°F), the amount of mzz(E) formed would be about 4% by weight (800 ppm/day times 50 days). Using 300 ppm of the mzz(E) per day formed at 200°C (392°F), the amount of mzz(E) formed would be about 3.5% by weight (300 ppm/day times 115 days).

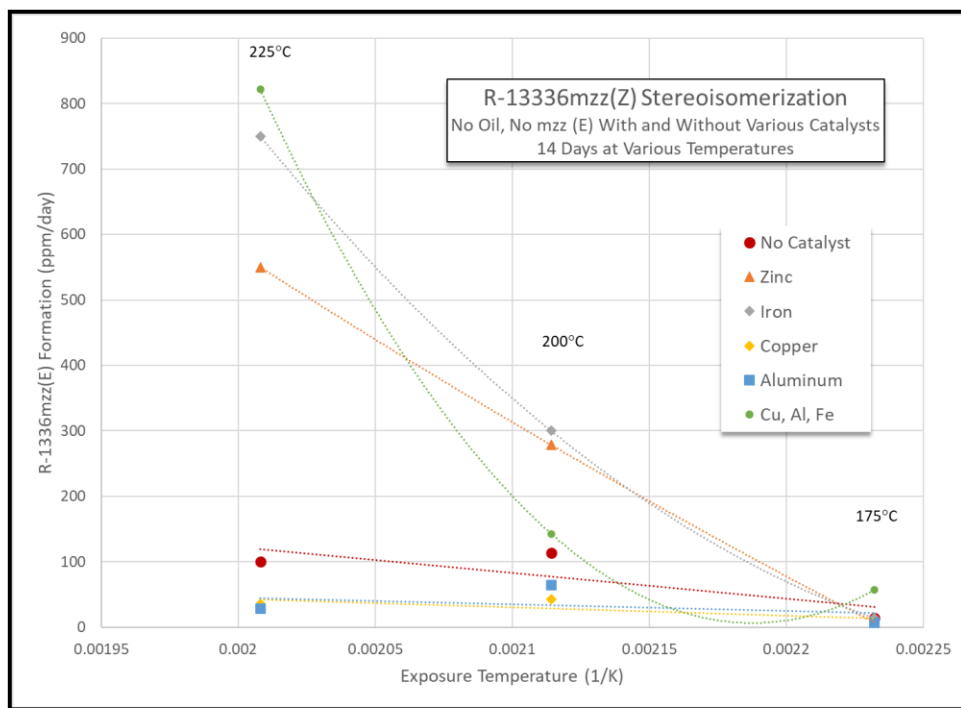


Figure 3. Summary of R-1336mzz(Z) Stereoisomerization Conversion Rates

3.2 Study of R-1336mzz(E) Stereoisomerization Rates

The mzz(Z) experimental process was repeated with pure mzz(E). Sealed glass tubes were prepared and exposed for 14 days at 175°C (347°F), 200°C (392°F), and 225°C (437°F). Figure 4 provides a summary of the results in parts per million (ppm) of the mzz(Z) isomer produced per day with and without various catalysts.

As expected, essentially no mzz(Z) isomer was formed with any of the catalysts or at any temperature since the mzz(E) isomer is more stable than the mzz(Z) isomer. Even though the no catalyst and the Cu/Al/Fe catalyst experiments showed about 200 ppm or 14 ppm/day formed at all the temperatures, these results are statistically insignificant since the analytical results are near the quantitation limit of 100 ppm.

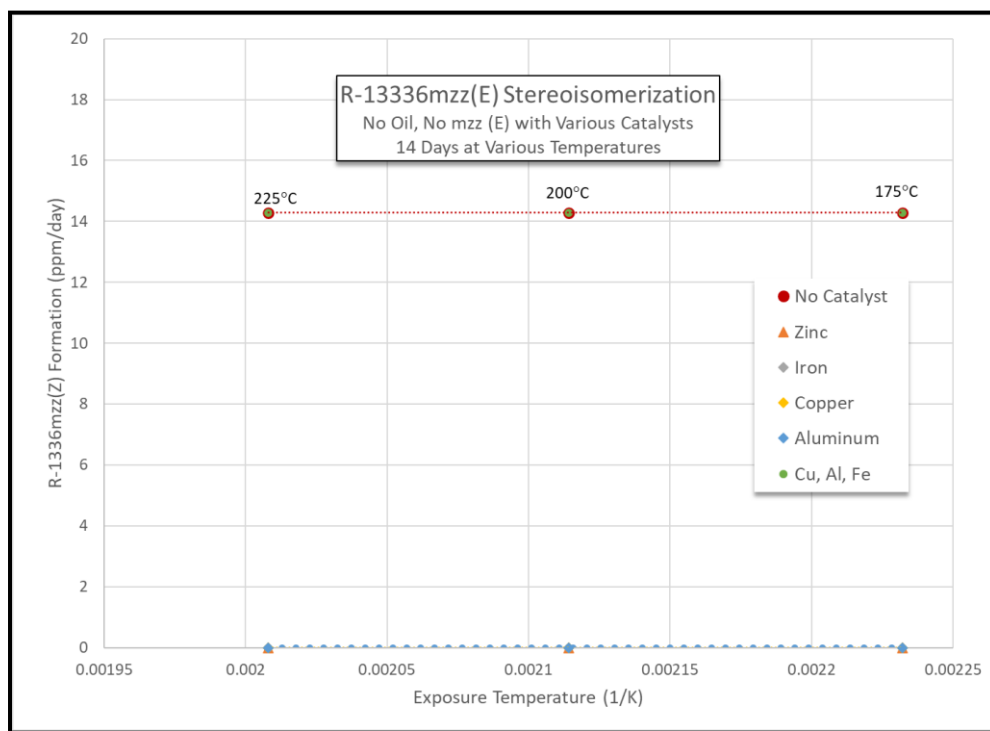


Figure 4. Summary of R-1336mzz(E) Stereoisomerization Conversion Rates

3.3 Impacts of R-1336mzz(Z) and R-1336mzz(E) Concentrations on Stereoisomerization Rates

A series of experiments were conducted with a blend of approximately equal amounts (50%/50% by weight) of both the mzz(Z) and mzz(E) isomers. Figure 5 provides a summary of the results in parts per million (ppm) of the mzz(E) isomer produced per day with and without various catalysts.

Unexpectedly, the mzz(E) isomer depleted and mzz(Z) isomer increased in the presence of aluminum, copper, iron, zinc catalysts, including the no catalyst exposure. Only the three-metal catalyst (Cu, Al, Fe) showed conversion rate to the mzz(E). These results may indicate that the concentration of the reactants and products is a factor in the stereoisomer reaction rates, which is an input for first order chemical reactions. It was expected that the mzz(E) would form preferentially to the mzz(Z), because the mzz(E) or trans-isomer is less sterically hindered than the mzz(Z) or cis isomer. What was unexpected in most experiments was that the stereoisomerization went in the opposite direction of favored trans-isomer, and the mzz(Z) was formed at higher concentrations than the mzz(E). More work is required to understand this outcome, including repeating this work at various concentrations of mzz(E&Z), as well as reviewing analysis procedures and developing process control practices to ensure accuracy of the results.

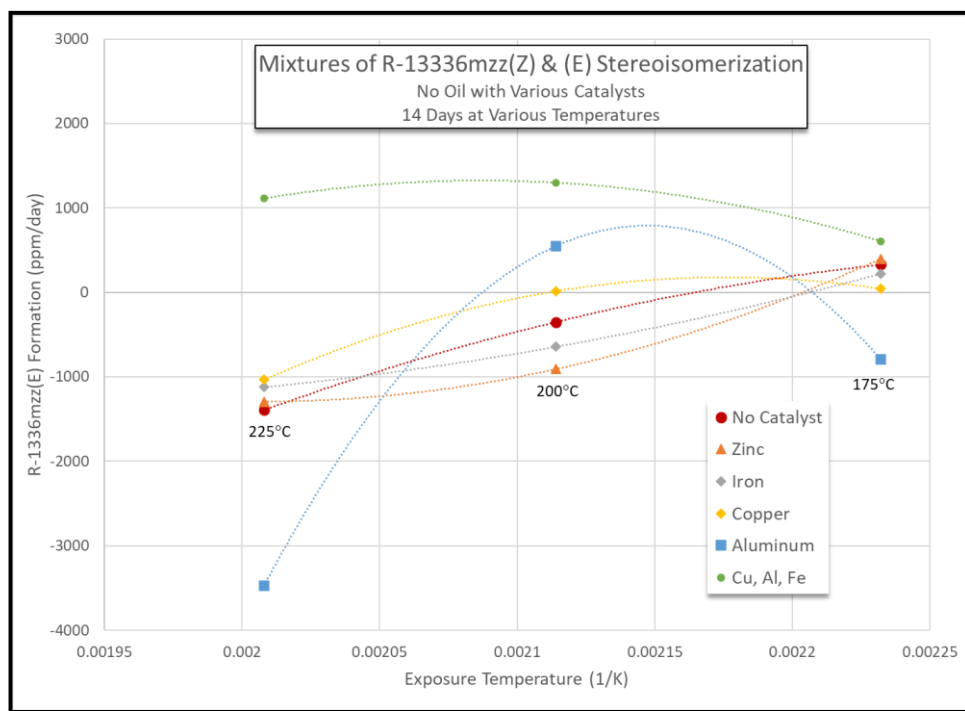


Figure 5. Summary of R-1336mzz(E) Stereoisomerization Conversion Rates in a 50%/50% by Weight Blend of Both Isomers

3.4 Study of R-1233zd(E) Stereoisomerization Rates

Pure or 100% R-1233zd(E) was studied with and without a combination of copper/aluminum/iron catalysts. In addition, zd(E) was evaluated in the presence of various lubricants with and without a combination of copper/aluminum/iron catalysts. Two mineral oil lubricants (no additive) and a polyolester (POE) lubricant with and without additives were evaluated to understand their impact on zd(E) stereoisomerization. The lubricants evaluated are summarized in Table 1. The zd(E), as received, did not contain a measurable amount of the zd(Z) isomer (<100 ppm). Sealed glass tubes were prepared and exposed for 14 days at 200°C (392°F), and 230°C (446°F). Figure 6 provides a summary of the results in parts per million (ppm) of the zd(Z) isomer produced per day.

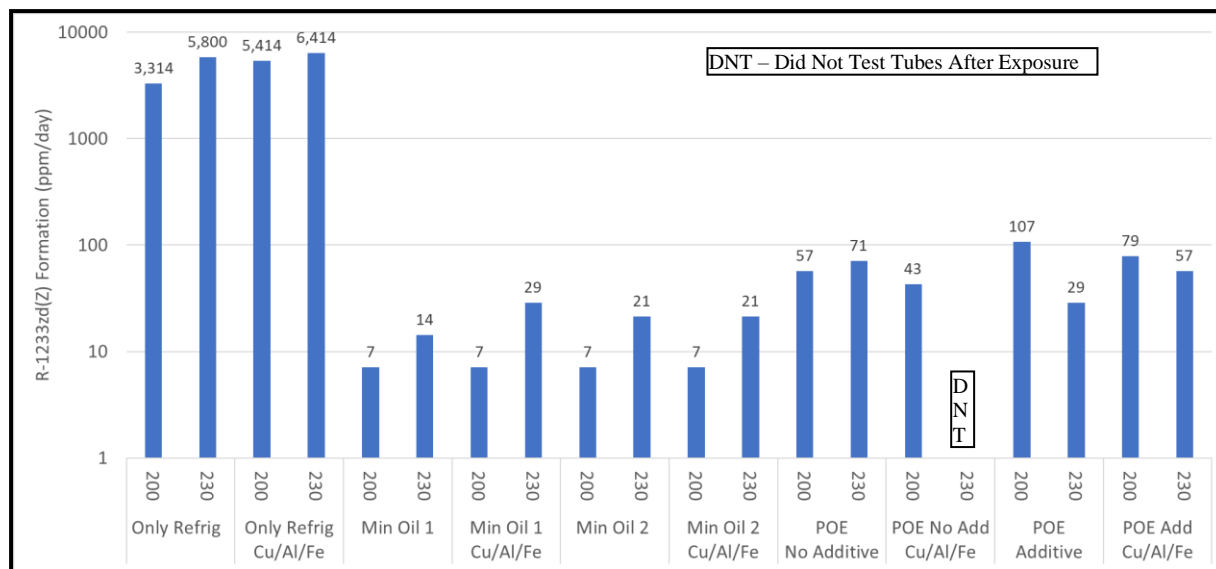


Figure 6. Summary of R-1233zd(E) Stereoisomerization Conversion Rates

Since the “E” isomers are generally thermodynamically favored over the “Z” isomers, it was expected that the amount of zd(Z) formed would be like what was seen with the mzz(E) experiments where little or no stereoisomer rearrangement to the mzz(E) occurred at any temperature or in the presence of catalyst. In this case, significant amounts of stereoisomer rearrangement to the “Z” isomer were seen in pure refrigerant with and without catalysts.

This stereoisomerization rearrangement rate was 10 times higher than the mzz(Z) stereoisomer rearrangement experiments, which was a surprising result. Using the previously discussed Arrhenius modeling with a conversion rate of 3300 ppm of the zd(Z) per day at 200°C (392°F), the amount of zd(Z) formed would be greater than 35% by weight (3300 ppm/day times 115 days) over 10 years. Using the three-metal catalyst result, this equates to greater than 60% by weight zd(Z) formed over 10 years (5400 ppm/day). This would have a significant effect on equipment operation. R-1233zd(E) has a boiling point of roughly 18°C (64°F) and R-1233zd(Z) has boiling point of 39°C(102°F), which would reduce the capacity of the equipment significantly over time as R-1233zd(Z) forms.

Fortunately, the addition of lubricant to the experiments had a very strong suppression of the stereoisomer conversion rate. The stereoisomer rate was suppressed by the order of 1000 fold with the mineral oil and POE lubricant exposures compared to the pure refrigerant exposures. The suppression of the stereoisomerization was regardless of the three metal catalysts or the presence of the POE additive. POE lubricant was more reactive in general than the mineral oil. In one case, the POE with no additive and no three-metal catalysts at 230°C (446°F) condition was so discolored, the tubes were not evaluated after exposure because of concern with damage to the GC-TCD instrumentation.

4. CONCLUSIONS

This paper provides some of the first investigations into the stereoisomer rates for R-1336mzz(Z), R-1336mzz(E) and R-1233zd(E), which are being considered or are being used in very high temperature heat pumps (VHHP). Three series of experiments were conducted with the R-1336mzz stereoisomers: 100% R-1336mzz(Z), 100% R-1336mzz(E), and roughly a 50/50 mixture by weight of both isomers with and without various catalysts were tested at various temperatures for 14 days. The R-1233zd(E) experiments were conducted with 100% R-1233zd(E) with and without various lubricants, catalysts, and test temperatures for 14 days.

The following observations were seen with stereoisomerization of the R-1336mzz isomers:

- As expected, the R-1336mzz(E) is the more thermodynamically stable isomer since no significant amount of R-1336mzz(Z) formed in the pure R-1336mzz(E) experiments at any temperature with or without any of the evaluated catalysts.
- R-1336mzz(Z) stereoisomer rearrangement was observed in almost all exposures. Iron and zinc are catalysts that can accelerate the stereoisomerization rate with the R-1336mzz(Z) isomer to form the more stable R-1336mzz(E) isomer.
- Unexpectedly, a 50/50 blend of the two isomers showed that the R-1336mzz(E) depletes and the R-1336mzz(Z) concentration increases in most of the experiments, which indicates that the stereoisomerization reaction may be concentration dependent and there might be an equilibrium concentration that can be reached between the isomers.
- In general, the mzz stereoisomers had good stereoisomer rearrangement stability at the elevated temperatures, but more work is needed to understand other potential catalysts that can drive stereoisomer rearrangement reaction, especially with the R-1336mzz(Z).

The following observations were seen with stereoisomerization of the R-1233zd(E):

- Even though the R-1233zd(E) is the more thermodynamically stable isomer, the R-1233zd(Z) still formed in the 100% R-1233zd(E) exposures with or without catalysts. In this case, the conversion rate was about 3300 ppm per day at 200°C (392°F) compared to the mzz(Z) to the mzz(E) isomerization rate at the same conditions of 150 ppm per day, respectively. The R-1233zd(E) stereoisomerization rearrangement rate was about 20 times higher than the R-1336mzz(Z) rate.
- The three metal catalysts accelerated the stereoisomer conversion rate in pure R-1233zd(E) exposures.
- Lubricant has very strong suppression of the stereoisomer rearrangement rate. Both the mineral oil and POE lubricant can reduce the pure refrigerant rates by greater than 1000-fold. The suppression of the stereoisomerization is regardless of the three metal catalysts or if the POE additive is present.

- In general, the R-1233zd(E) stereoisomer had good stereoisomer rearrangement stability in the presence of lubricant at the elevated temperatures, but its stability for use in a lubricant free environment would need to be questioned. More work is needed to understand other potential catalysts or what is driving stereoisomer rearrangement instability with no lubricant present.

These studies offer a first glimpse at understanding the stereoisomer rearrangement potential and the chemistry of HFOs and HCFOs. More work is required to understand fully the HVACR equipment reliability impacts.

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NOMENCLATURE

mzz(Z)	R-1336mzz(Z)	zd(Z)	R-1233zd(Z)
mzz(E)	R-1336mzz(E)	ppm	Parts per million
HCFO	Hydrochlorofluoroolefin	HFO	Hydrofluoroolefin
zd(E)	R-1233zd(E)	K	Kelvin
R	Rankine		

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