



Studies on Hexafluoropropene Dimer Isomerization

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Abstract

Hexafluoropropylene dimer serves as a representative template for the synthesis of various fluorinated substances. Isomerization of two dimers is an important reaction. The changes in single-point energies for isomerization were calculated, and it was found that the most stable compound is Perfluoro(2-methylpent-2-ene) with a single-point energy of -3745686.47 KJ/mol. The kinetics of hexafluoropropene dimer isomerization were experimentally investigated in the temperature range of 303 - 343 K using KF and 18-crown-6 as catalysts. The activation energy ($E = 76.64$ kJ/mol) was calculated. The reaction kinetics equation can be expressed as $r = 4.14 \times 10^{11} \exp(-9217.7/T) C_{D-1}$. The simulation results for both thermodynamics and kinetics showed good agreement with the experiment.

Subject Areas

Chemical Engineering & Technology

Keywords

Hexafluoropropylene, Dimer, Isomerization, Perfluoro(2-Methylpent-2-Ene), Simulation

1. Introduction

Hexafluoropropene (HFP) oligomers, which consist of two dimers, namely Perfluoro(4-methylpent-2-ene) (D-1) (CAS: 2070-70-4) and Perfluoro(2-methylpent-2-ene) (D-2) (CAS: 1584-03-8), have been recognized for their applications as solvents with excellent thermal and chemical stability. Among perfluoroalkyl compounds, HFP oligomers are particularly versatile and can undergo further chemical modifications [1] [2] [3]. **Figure 1** shows the structure of D-1 and D-2.

These isomers have different uses due to variations in solubility in organic

solvents and chemical stability, particularly their reactivity towards nucleophilic reagents. Therefore, it is desirable to obtain these isomers as individual compounds, chosen based on their intended use, or as a mixture where the majority component is the desired isomer. Among the oligomers mentioned, the D2 isomers are particularly useful due to their higher thermodynamic stability and chemical reactivity. For example, the D2 isomer can react with phenol in the presence of triethylamine as a condensation reagent to produce perfluorohexynylphenyl ether, an important intermediate in surfactant production [4] [5]. It is an important process of isomerizing D1 into thermodynamically stable isomers D2 (**Figure 2**).

The isomerization of perfluor-olefins can be achieved by generating carbon cations through the use of reagents such as SbF_5 or KF . The addition of a “crown ether” to the reaction mixture enhances the catalytic activity by strongly coordinating the cation of a dissociable compound, such as an alkali metal halide, and activating the corresponding anion [6] [7]. Crown ethers are macrocyclic ethers that can have oxygen atoms partially substituted with nitrogen, sulfur, and/or phosphorus. Their ability to coordinate with cations promotes the dissociation of alkali metal fluorides and enhances the nucleophilic behavior of their anions. This synergistic effect between alkali metal fluorides and crown ethers is the key to their remarkable catalytic ability [8] [9] [10].

In this paper, we present a thermodynamics study of the isomerization. A particular effort has been devoted to understanding the kinetics of the reaction. Understanding the thermodynamics and kinetics of a reaction is crucial for gaining a deeper understanding of the nature of chemical reactions and for mastering aspects such as optimizing reaction processes and engineering design.

2. Experimental Section

2.1. Experimental Setup

A three-necked round-bottom flask with mixing capability and a well-controlled temperature system can be used as a reactor for the experiment.

2.2. Experimental Methods

10 ml of acetonitrile was added to the flask, 3 g of D1 was added to the flask,

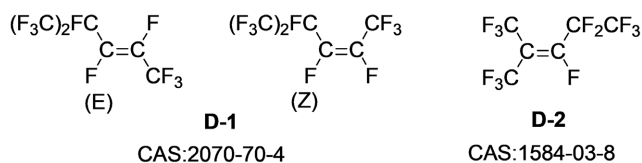


Figure 1. Structure of D-1 and D-2.

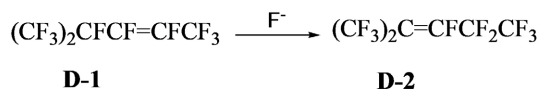


Figure 2. Isomerizing D1 into D2.

followed by 0.002 g of KF and 0.065 g of 18-crown-6. The flask was then tightly sealed and placed in a water bath set at a specific temperature with a precision of $\pm 0.2^\circ\text{C}$. The composition of the oligomer phase in the flask was analyzed using gas chromatography. The GC inlet temperature was set at 150°C to prevent the condensation of liquid products. The products were injected through the sample loop, which was controlled by a high-temperature ten-port valve. The GC oven was initially held at 40°C for 5 minutes and then ramped up to 120°C at a rate of 40°C per minute.

3. Results and Discussion

3.1. Single-Point Energies Changes for Isomerization

D-1 and D-2 structures were fully optimized by B3LYP method at 6-31G (d) basis set. The single-point energies were calculated by using Gaussian 16 programs package (Figure 3).

Single point energy difference between the E and Z isomer is $10.03\text{ kJ}\cdot\text{mol}^{-1}$. The single-point energy difference between the E and Z isomers is calculated to be $10.03\text{ kJ}\cdot\text{mol}^{-1}$. The theoretical calculations also indicate an energy barrier of $31.86\text{ kJ}\cdot\text{mol}^{-1}$ for the isomerization process. These values are in good agreement with the experimental results, which show a similar difference in thermal energy. Thus, it can be concluded that D1 has the ability to undergo isomerization into the isomer D2, twice as much as a purely theoretical calculation.

3.2. Kinetic Modelling

A kinetic model was developed for the isomerization of hexafluoropropene dimer. The D1 isomer converts to D2 through a successive reaction, without any

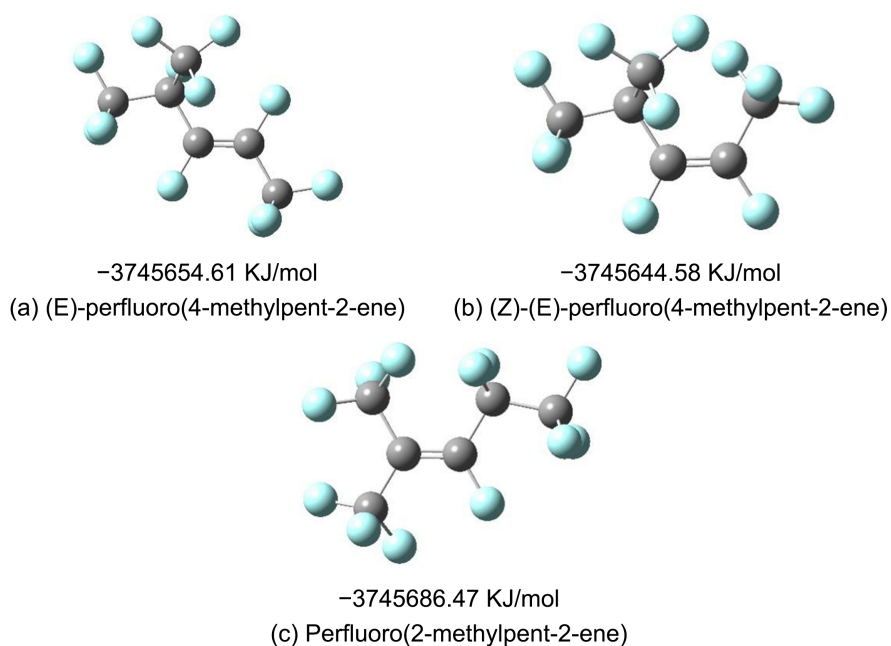


Figure 3. Single-point energies of D-1 and D-2.

byproduct formation (**Figure 4**). The experiment was conducted under isothermal conditions, as no temperature change was observed throughout the reaction. Additionally, it was assumed that the reaction is not limited by diffusion. Considering these assumptions, the following rate equations can be written for scheme 1:

$$r = -\frac{dC}{dt} = kC^n \quad (1)$$

It was assumed that the D1 isomerizes to D2 is of first order.

$$C = C_0 \exp(-kt) \quad (2)$$

$$-\ln(1-x) = kt \quad (3)$$

$-\ln(1-x)$ plots time to get a straight line. The slope of the straight line is the reaction rate constant at this temperature, show in **Figure 5**. See **Table 1** for data of fitting curve.

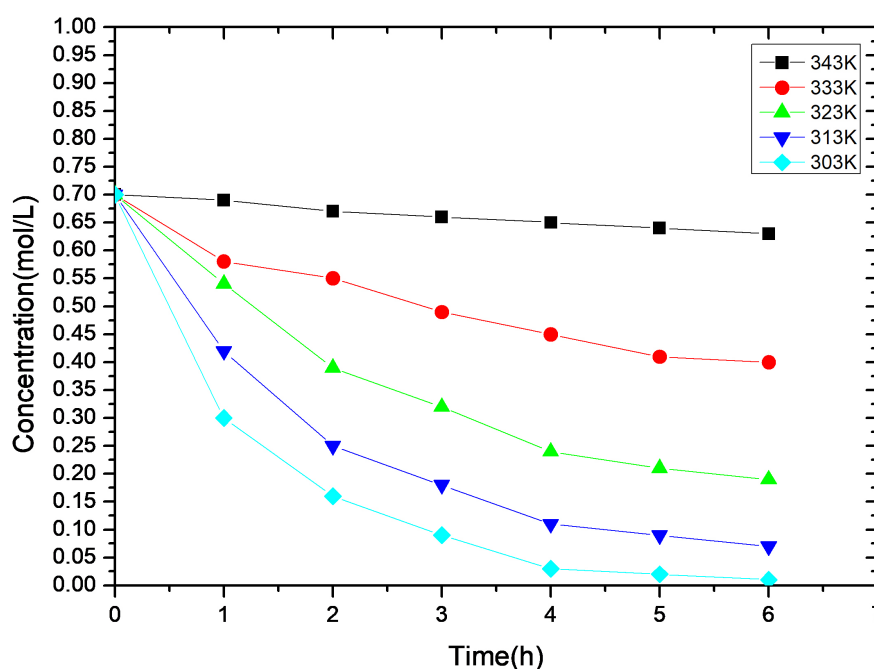


Figure 4. The changes of D1 concentration with time.

Table 1. Fitting data of $-\ln(1-x)$ and.

Temperature(K)	rate constant k/h^{-1}	R^2
303	0.01774	0.99
313	0.09190	0.98
323	0.22452	0.98
333	0.38606	0.99
343	0.70484	0.99

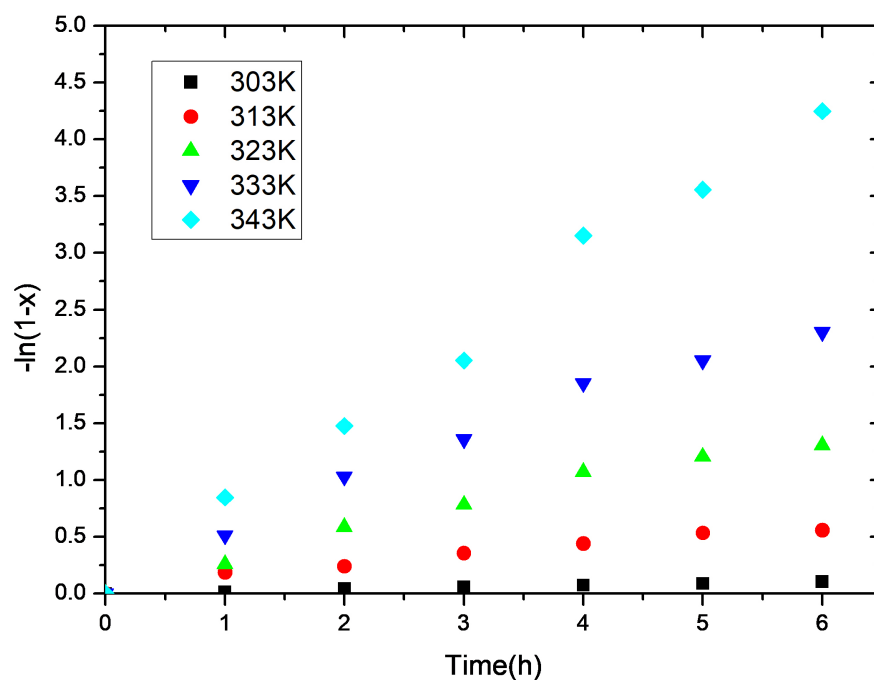


Figure 5. Fitting results of $-\ln(1-x)$ and time.

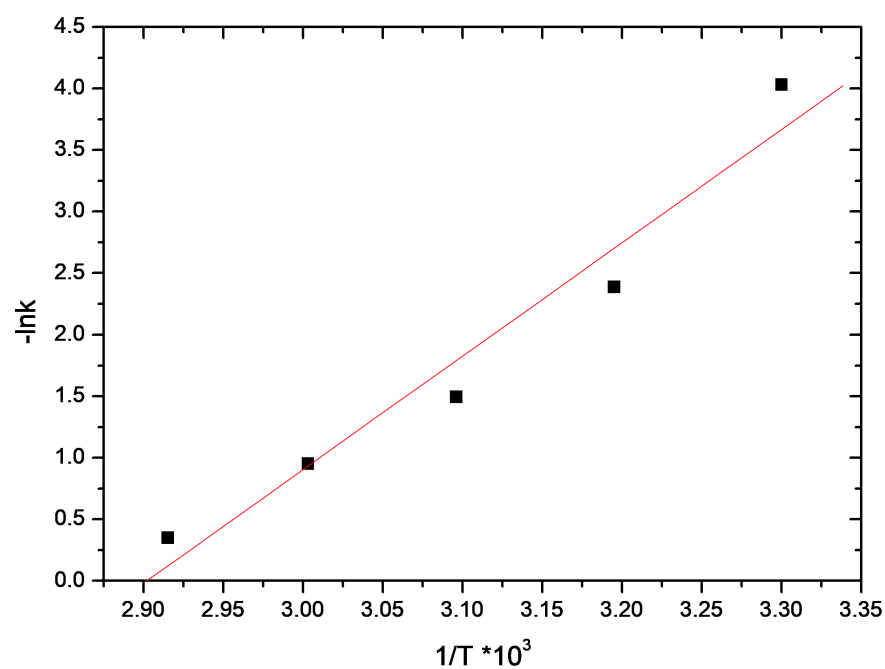


Figure 6. Fitting results of $-\ln k$ and $1/T$

The activation energy of isomerization of D-1 is related to the temperature dependent rate constant (k) according to the Arrhenius equation given below:

$$k = A \exp(-E_a/RT)$$

$$-\ln k = \frac{E_a}{RT} - \ln A$$

$$E_a = 76.64 \text{ KJ}\cdot\text{mol}^{-1},$$

$$r = 4.14 \times 10^{11} \exp(-9217.7/T) C_{D-1}$$

Figure 6 shows the fitting results of $-\ln k$ and $1/T$. By the action of KF at high temperature, a part of dimer was isomerized into thermodynamically more stable dimer. The activation energy of isomerization of D-1 is $76.64 \text{ KJ}\cdot\text{mol}^{-1}$.

4. Conclusions

We report herein that thermodynamic and kinetic isomerization of hexafluoropropene dimer.

The theoretical calculations also indicate D1 has the ability to undergo isomerization into the isomer D2, an energy barrier of $31.86 \text{ kJ}\cdot\text{mol}^{-1}$ for the isomerization process.

The kinetics of D-1 isomerization was successfully investigated using KF and 18-crown-6 as catalysts. Kinetic model was developed for the isomerization of hexafluoropropene dimer, and the activation energy was estimated to be 76.64 KJ/mol .

It is worth mentioning that the use of ion-fluoride as a catalyst for isomerization processes has wide applicability and offers the possibility of synthesizing perfluoroolefins with different structures. These processes have clear advantages and real potential for implementation in industrial technologies.

Conflicts of Interest

The author declares no conflicts of interest.

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