Mechanism of Formation of Trans Fatty Acids under Heating Conditions in Triolein

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ABSTRACT: To elucidate the relationship between heat-induced cis/trans isomerization and reaction temperature and energy in unsaturated lipids, we investigated the molecular mechanism of the heat-induced cis/trans isomerization of 18:1 isomers. Triolein (18:1,9c) was heated at two range temperatures (130, 160, 190, 220 °C and 135, 140, 145, 150, 155 °C) and analyzed by the gas chromatography (GC) method. When the heating temperature increased to 150 °C, the amount of trans 18:1n-9 changed from 0.0897 mg/g oil (1 h) to 0.1700 mg/g oil (3 h). This study shows that the cis to trans isomerization may occur at 150 °C. The formation of fatty acid isomers followed a proton transfer route. All key geometries, transition states, intermediates, and bond dissociation energies (BDE) were optimized at the B3LYP/6-31G* level for the density functional theory (DFT). The zero-point energy corrections of the isomers were carried out using calculations at the B3LYP/6-311++G** level. The calculated energy difference between the cis and trans oleic acid was equal to 7.6 kJ/mol, and the energy barriers of the transition from cis 18:1n-9 to trans 18:1n-9 were 294.5 kJ/mol. The intrinsic reaction coordinates (IRCs) were obtained to be used as an expression of the reaction route and to analyze the transition states and intermediates. The study results suggest that the heating temperature should be kept under 150 °C, to avoid the risk of trans fatty acid (TFA) intake in daily food.

KEYWORDS: triolein, trans fatty acids, isomerization, density functional theory, energy barriers

INTRODUCTION

Trans fatty acids are present in many kinds of foods and dietary supplements. They are mainly produced from hydrogenation and deodorization processes and are also derived from deep frying. Some researchers have shown that trans fatty acids could elevate levels of serum low density lipoprotein cholesterol and lower high density lipoprotein cholesterol levels.[1−4] Partially hydrogenated edible oils have been reported to present a risk factor that could cause coronary heart disease.[5]

Oleic acid mainly exists in camellia oil, peanut oil, olive oil, and coconut oil with the form of triolein, which has a very large proportion of unsaturated fatty acids. Oleic acid is one of the simplest unsaturated fatty acids and the heat-induced cis/trans isomerization of triolein is essentially the isomerization of oleic acid; therefore, 18:1 is ideal to be used to assess the fatty acid isomerization and decomposition. Previous studies have reported that metals (e.g., nickel) and free radicals (e.g., thiyl radical) could catalyze the isomerization of C=C double bonds during the hydrogenation process.[6] However, there is very limited information about the mechanism of heat-induced isomerization of double bonds in unsaturated fat without catalysts. Previous studies showed that the π bond of the C=C double bond should clearly be broken before the isomerization rotation,[7] and hydrogen migration along with the breakage of the π bond is supposedly easier.[8] The energy requirement and mechanism of fatty acid cis/trans isomerization have not been fully studied, and a better understanding of this mechanism is much needed.

Density functional theory (DFT) is widely used in physics and chemistry, especially to study the properties of molecules and predict properties of chemical systems. This method has been used to study functional properties of linoleic acid.[8] The purpose of the present work is to determine the energy requirement and the cis/trans isomerization mechanism of triolein under thermal treatment. The isomerization products of triolein upon thermal treatment at various conditions were determined by gas chromatography (GC). DFT was then used to confirm the isomerization of lipids by theoretical calculations to obtain the geometric parameters of the ground and transition states of cis/trans isomers and to investigate the reaction process of cis/trans isomerization of 18:1.

MATERIALS AND METHODS

Materials. The 37-component FAME mix was purchased from Sigma-Aldrich (Bellefonte, PA, USA). Methyl elaidate was purchased from NU-CHEK Prep, Inc. (Elysian, MN, USA). Triolein was purchased from NU-CHEK Prep. Hexane obtained from Concord Scientific Co. Ltd. (Tianjin, China) was used as a chromatographic organic solvent.

Thermal Analysis. The temperatures and heat flows associated with transition were measured using a differential scanning calorimetry (model DSC-60A, Shimadzu, Japan). Approximately 3−5 mg of the triolein sample was placed in an aluminum sample pan. The sample pan was then placed on the sample platform, while an empty aluminum pan was placed on the reference platform. To determine the temperature of isomerization transition of the triolein sample, a linear heating rate of 5 °C/min over a temperature range of 100−200 °C was used.

Preparation of Sample. Triolein (about 1 g) was transferred to a 10 mL glass vial and heated in methyl silicon oil bath for 1 and 3 h at 130, 160, 190, 220 °C, and 135, 140, 145, 150, 155 °C, respectively.

The accuracy of temperature control during oil heating was ± 1 °C. The heated samples were stored at −20 °C under nitrogen.

Preparation of FAMEs. Fatty acid methyl esters (FAMEs) were prepared according to a developed method described in a previous report.[9] A total of 20 mg of oils was weighed in a sealable glass tube, and 4 mL of 2% concentrated sulfuric acid/methanol (v/v) was added. The sealable glass tube was placed in a water bath temperature of 80 °C for 2 h, and then 2 mL of distilled water and 2 mL of hexane were added after the glass tube cooled in water. For extraction, the mixture was stirred for 2 min, the hexane phase was removed, and approximately 1 g anhydrous sodium sulfate was added and analyzed by GC.

Analysis of Fatty Acid Methyl Esters. The analysis of FAMEs was carried out using a Shimadzu (Tokyo, Japan) GC-14B instrument equipped with a flame ionization detector (FID). A fused-silica capillary column HP-88 (100 m × 0.25 mm i.d., 0.20 μm film thickness, Agilent Corp., Palo Alto, CA, USA.) was used for the separation of FAME. Nitrogen was used as the carrier gas at a column pressure of 420 kPa (20 °C); the split ratio was 55:1 and the detection limit was 2.00 mg/L for oleic acid and elaidic acid. The temperatures of the injector and detector were set at 230 and 250 °C. The analysis was carried out using a temperature gradient program from an initial temperature at 120 °C and held for 4 min, then programmed to 175 °C at 10 °C/min and held for 6 min, and then programmed to 210 °C at 5 °C/min and held for 5 min. Finally, the temperature was increased to 230 °C at a rate of 4 °C/min and held at 230 °C for 30 min. FAMEs were identified by retention time comparison with that of the corresponding standards.

GC Calculation. The amount of cis 18:1n-9 and trans 18:1n-9 in each test sample were calculated according to eqs 1 and 2, respectively.

$$W_i = \frac{A_i - 5066.45}{158.35} \times \frac{V_i \times 1.0046}{1000 \times m_i} \times \frac{M_{FAi}}{M_{FAMEi}} \tag{1}$$

where $y = 5066.45 + 158.35x$ is the standard curve equation of cis 18:1n-9, W_i is the weight of fatty acid (FA) i in the sample, A_i is the peak area of the individual FAME i in the sample, V_i is the volume of solvent in the sample, m_i is the weight of triolein in the sample, 1.0046 is the conversion coefficient between triolein and FAME 18:1, M_{FAi} is the molecular weight of FA i, and M_{FAMEi} is the molecular weight of FAME i.

$$W_k = \frac{A_k - 91.75}{133.81} \times \frac{V_k \times 1.0046}{1000 \times m_k} \times \frac{M_{TFAk}}{M_{TFAMEk}} \tag{2}$$

where $y = 91.75 + 133.81x$ is the standard curve equation of trans 18:1n-9, W_k is the weight of TFA k in the sample, A_k is the peak area of the individual trans fatty acid methyl ester (TFAME) k in the sample, V_k is the volume of solvent in the sample, m_k is the weight of triolein in the sample, 1.0046 is the conversion coefficient between triolein and FAME 18:1, M_{TFAk} is the molecular weight of TFA k, and M_{TFAMEk} is the molecular weight of TFAME k.

Computational Methods. All calculations were performed using the Gaussian 09 W software (Gaussian, Inc.)[10] supplied by College of Chemistry, Nankai University. The calculations of stable optimization geometries and bond dissociation energy (BDE) were based on density functional theory (DFT) with Becke's 3 parameters (B3) and the Lee−Yang−Parr's nonlocal correlation functional (LYP) functional at the 6-31G* level. Zero-point energy corrections of each isomer was calculated at the B3LYP/6-311++G** level. IRCs were obtained to examine all the transition states and intermediates.

BDE is defined as

$$BDE = H(R^\bullet) + H(H^\bullet) - H(R-H) \tag{3}$$

where $H(R^\bullet)$ is the total enthalpy of the radical, $H(H^\bullet)$ is the total enthalpy of the abstracted hydrogen atom, and $H(R-H)$ is the total enthalpy of the molecule. In the case of the DFT method, the total enthalpies of the species X, $H(X)$, at temperature T are estimated from the expression

$$H(X) = E_0 + ZPE + \Delta H_{trans} + \Delta H_{rot} + \Delta H_{vib} + RT \tag{4}$$

where E_0 is the calculated total electronic energy, ZPE represents zero-point energy, ΔH_{trans}, ΔH_{rot}, and ΔH_{vib} are the translational, rotational, and vibrational contributions to the enthalpy. Finally, RT stands for the PV work term, which is added to convert the internal energy, U, to the enthalpy $(H = U + PV)$.[11]

Statistical Analyses. All the experiments were performed in triplicate. For calibration of the assays, method of linear regression analysis was applied by plotting the response area and concentration. The slope, intercept, and correlation coefficient (R^2) were measured by peak concentration and area. The data were analyzed using the Origin software (version 8.0724; Microcal Software Inc., Northampton, MA) and were presented as mean ± SD (standard deviation, $n = 3$).

RESULTS AND DISCUSSION

Thermal Analysis of Triolein. As shown in Figure 1, the DSC thermogram shows a small rather flat peak between 135
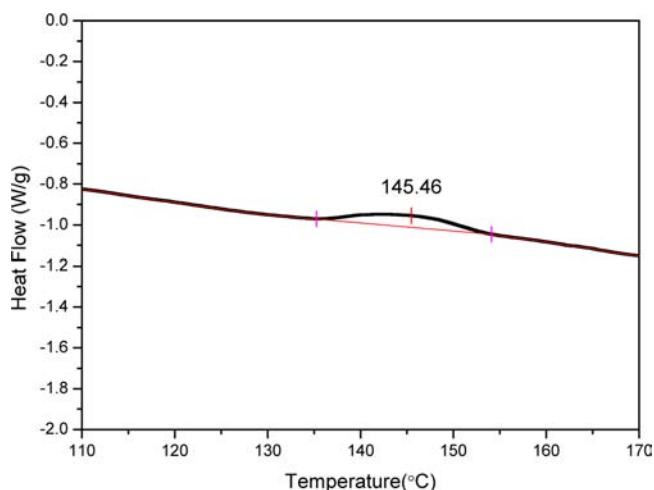

Figure 1. The DSC thermogram showing thermally induced point of isomerization of the triolein.

and 155 °C which could be attributed to the isomerization of oleic acid upon the breakage of the chemical bond. The reaction was thermally induced and accompanied by a small heat releasing. Such information is useful to access the starting point of oleic acid isomerization and to further determine a suitable temperature range for conducting cis/trans isomerization experiments.

Determination of 18:1 Isomers in the Heating Process. As shown in Figure 2, the 37-component FAME mix was separated by GC, and cis 18:1n-9 (peak 21) and trans 18:1n-9 (peak 22) could be clearly determinaed. In order to investigate the thermodynamics of heat-induced cis/trans isomerization and find the temperature inversion point in monounsaturated lipids, this work used a large temperature scale (130 °C, 160 °C, 190 °C, 220 °C), and in this temperature scale triolein (cis 18:1n-9; 1g) was heated for 1 and 3 h, respectively. The amount of cis and trans isomers in triolein are shown in Figure 3. No trans isomer was detected in the normal state. The level of cis 18:1n-9 was reduced from 100% to 8.89% and 7.16% when it was heated at 220 °C for 1 and 3 h, respectively. Small amounts of trans 18:1n-9 (0.1262 mg/g oil (triolein) and 0.3495 mg/g oil) were measured in the sample under 160 °C treated 1 and 3 h. Similar results have been reported by Tsuzuki,[11] who investigated the impact of heating on oleic acid isomers in triolein and trielaidin. Therefore, with the increase of temperature and heating time,
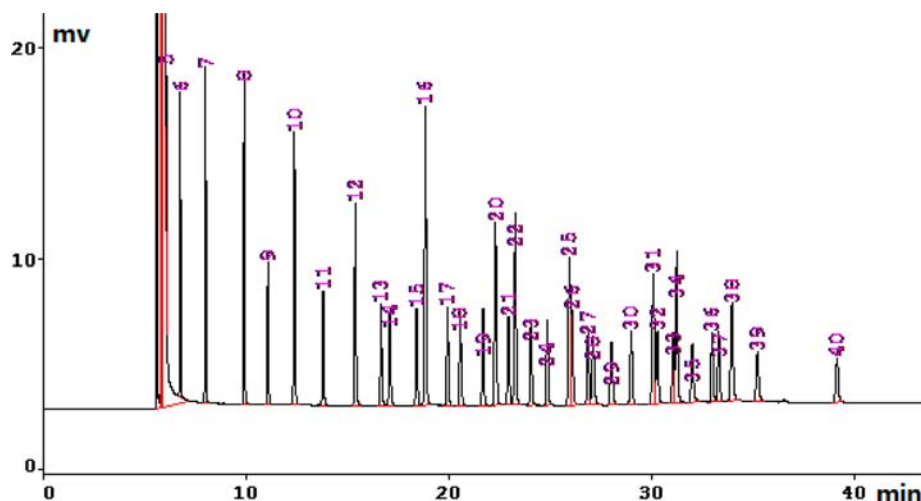
Figure 2. GC analysis of the 37-component FAME mix on an HP-88 fused-silica capillary column (100 m). Peak 21 and 22 were cis 18:1n-9 and trans 18:1n-9, respectively.
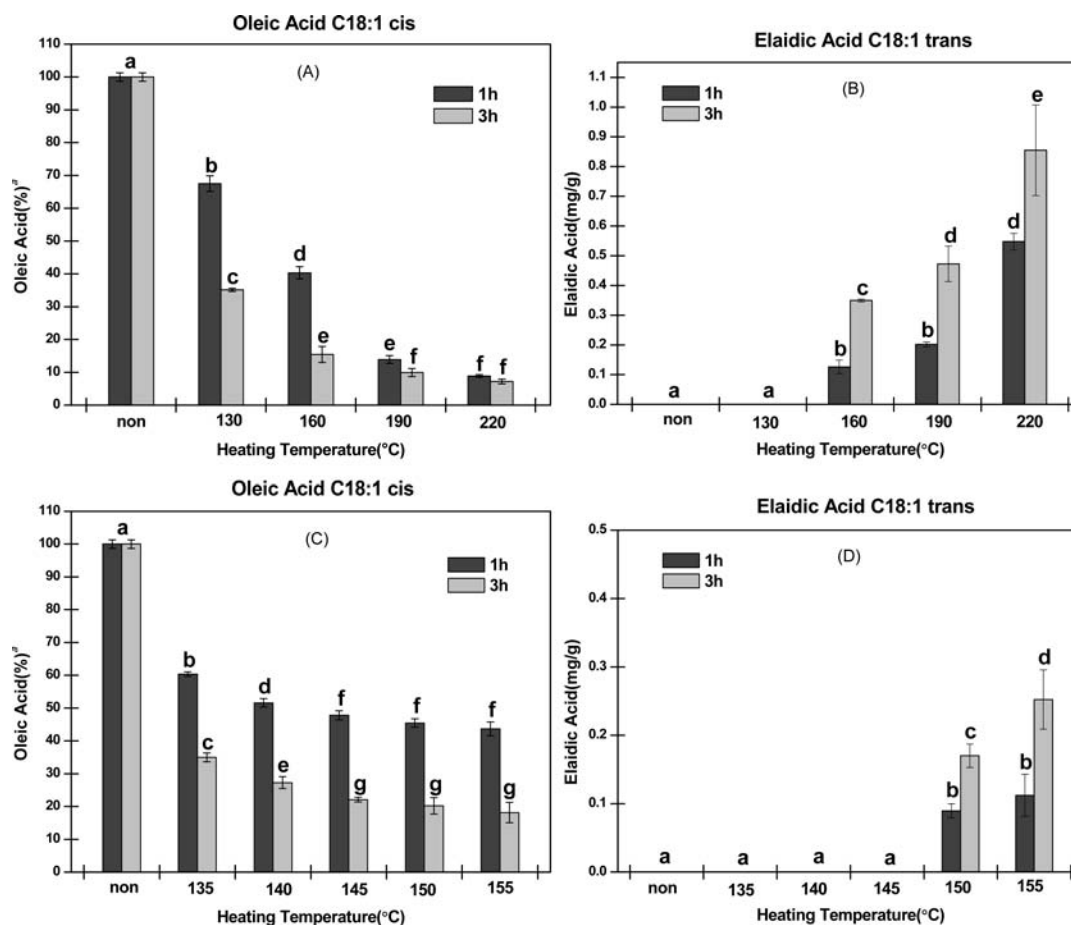

Figure 3. The amount of cis and trans isomers in triolein when 1 g of each triolein was incubated for 1 and 3 h at 130 °C, 160 °C, 190 °C, 220 °C (A and B) and 135 °C, 140 °C, 145 °C, 150 °C, 155 °C (C and D), respectively. The absolute amount of each isomer was calculated from the peak intensity of external standard (37 Comp.) FAME. The values represent the means ± SD of three times. The values at the temperature points not sharing common letters of an alphabet are significantly different ($P < 0.05$). The oleic acid measured was normalized to 100%.

the level of trans isomers increased gradually and isomerization started between 130 and 160 °C.

Then triolein sample was heated on a small temperature scale (135 °C, 140 °C, 145 °C, 150 °C, 155 °C) for 1 and 3 h, respectively, as shown in the Figure 3. The trans isomers was found at 150 °C, which indicated that the cis → trans

isomerization may started at 150 °C, and the amount of trans 18:1n-9 was from 0.0897 mg/g oil (heating 1 h) to 0.1700 mg/ g oil (heating 3 h). This result was in accord with the DSC analysis. Previous studies have reported the heat-induced isomerization of double bonds in unsaturated fatty acids, who investigated the isomerization of linoleic acid in soybean oil.[8] In
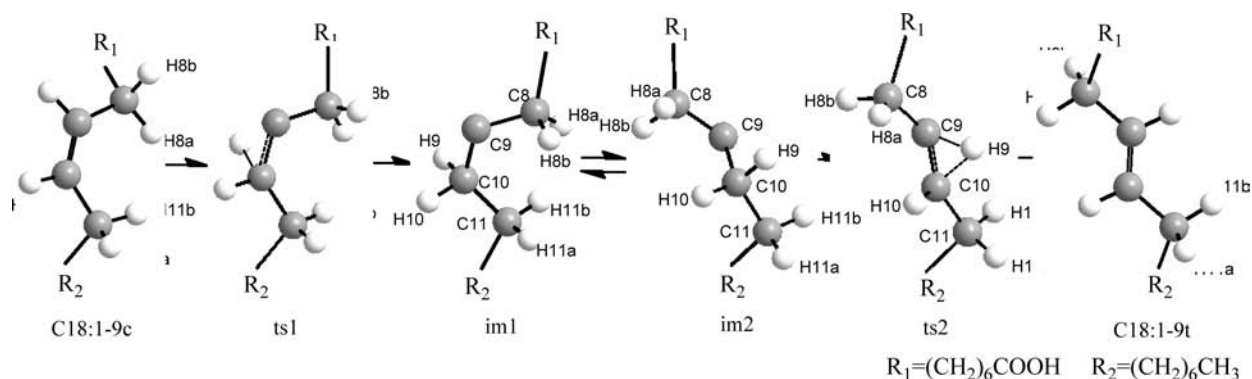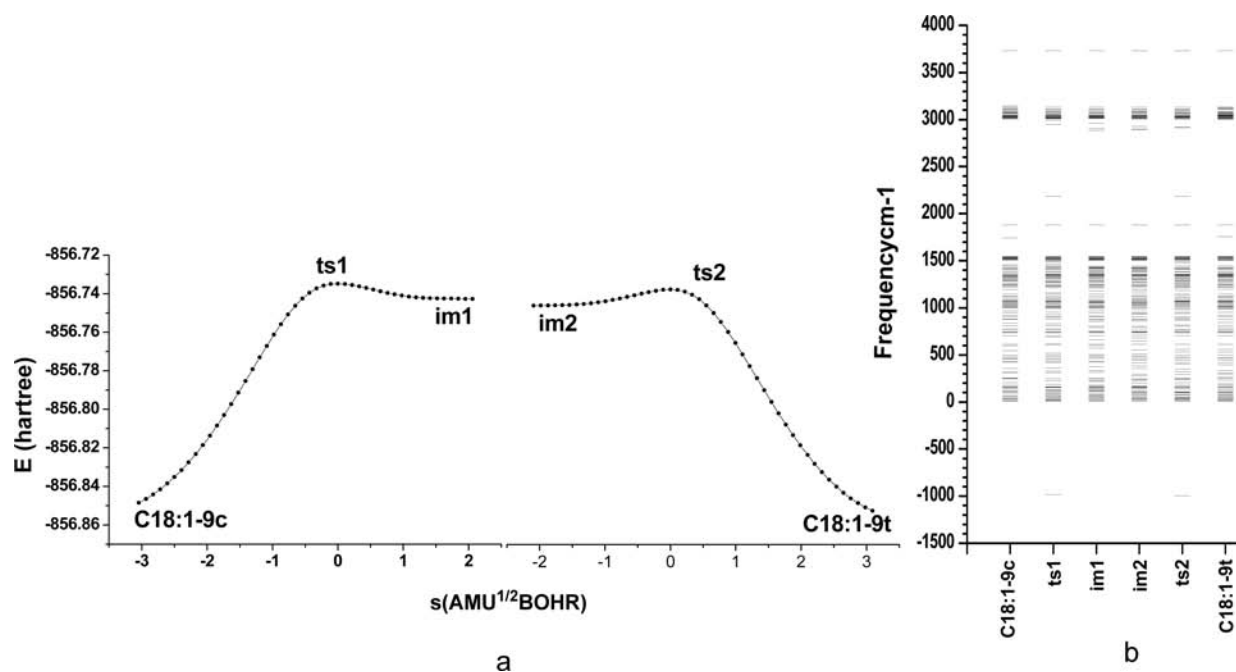
Figure 4. 18:1 isomerization scheme of the reactant cis 18:1n-9, transition states (ts), intermediates (im), and the product trans 18:1n-9.

Table 1. Optimum Geometry and C−C Bond Dissociation Energy (BDE) of Cis and Trans of 18:1 Isomers in the Ground Electronic State, As Calculated by the B3LYP/6-31G* Method

species	BDE (kJ/mol)			bond length (Å)			dihedral angle (deg)
	C8−C9	C9−C10	C10−C11	C8−C9	C9−C10	C10−C11	θ^a
cis 18:1n-9	395.8	687.5	394.6	1.506	1.339	1.506	0.409
trans 18:1n-9	402.3	694.4	401.5	1.505	1.336	1.505	179.705

^{a}Dihedral angle of C8−C9−C10−C11.

Figure 5. Energy (E) curves of the IRC isomerization reaction scheme (a) and frequencies for the reactant cis 18:1n-9, transition states (ts), intermediates (im), and the product trans 18:1n-9 (b). As observed, the transition states have one imaginary frequency.

this study, theoretically both oxidation and isomerization of triolein can occur simultaneously; however, through the GC analysis and the variation tendency of fatty acid, we found the formation of oxidation products could not obviously interfere with separation, identification, and quantitation of isomerized products of triolein. Consequently, the oil (e.g., camellia oil, peanut oil, olive oil, and coconut oil) heating temperature should be kept under 150 °C to avoid the risk of trans fatty acids intake in daily food.

Ground States of 18:1 Isomers. The isomerization of 18:1 and the experimental data were checked at the B3LYP/6-31G* level by performing DFT calculations. The cis isomer and

trans isomer have different structural features (see Figure 4 and Table 1). The optimized dihedral angles θ (C8−C9−C10−C11) for isomer cis 18:1n-9 and isomer trans 18:1n-9 were 0.409° and 179.705°, respectively. The optimized dihedral angle was in close proximity (<1°) to the ideal value (cis, 0°; trans, 180°) which indicated that the data were reasonable. Not only were the lengths of the trans C=C (1.336 Å) less than that of cis C=C (1.339 Å) but also the single bonds of C8−C9 (cis, 1.506 Å; trans, 1.505 Å) and C10−C11 (cis, 1.506 Å; trans, 1.505 Å) which were near the double bond and also showed a similar tendency. The BDE value could indicate the strength of bonding, which is fundamental to understanding

chemical processes.[12] The BDE value of trans C=C (694.4 kJ mol^{-1}) and cis C=C (687.5 kJ mol^{-1}) were in accord with the result of bond length which indicates that the trans isomer is more stable than the cis isomer.

The cis → trans isomerization process is a spontaneous process in theory. However, the reaction is difficult to carry out at room temperature or without any catalysts. The activation energies for isomerization of 18:1 and 18:2 are so high[8,13] that this reaction process needs more energy to go through energy barriers or reduce barrier heights significantly in order to allow the difficult reactions to occur easily. Previous studies have reported the fatty acid isomerization reaction in edible oils during the frying and heating process[14] and in sunflower seed oil with nickel catalysts.[15] In the study, the energies of 18:1 isomers were calculated and similar to the graphical presentation of the 18:2 isomers in the study of Christy.[16] The energy difference that was calculated between the cis and trans oleic acid was equal to 7.6 kJ/mol, which was much smaller than that of linoleic acid (13.2 kJ/mol).[8] The calculated energy difference between the cis and trans oleic acid was 7.6 kJ/mol, which was much smaller than that of linoleic acid (13.2 kJ/mol).[8] It is indicated that the trans structure of a molecule possesses stronger thermodynamic instability than a cis one. The energy barriers of the transition from cis 18:1n-9 to trans 18:1n-9 was 294.5 kJ/mol, which was larger than that of linoleic acid (284.2 or 286.4 kJ/mol).[8] Therefore, the isomerization of oleic acid is not easier than linoleic acid if treated with heat.

Isomerization Rotation of 18:1. Various calculations have been devised to obtain a good initial guess for the structures of transition states which was based on the breakage of π bond and the intermolecular proton transfer of the excited states under high temperature. Thus, a rotational isomerization scheme of the 18:1 transformation was researched, which was displayed in Figure 4. The scheme shows the isomerization process of cis 18:1n-9 → trans 18:1n-9 via two transition states (ts) and two intermediates (im). Only one imaginary (negative) frequency characterizes the transition states, which is used to verify the transition states, as shown in Figure 5b. The IRC results (Figure 5a) showed that the obtained minimum energy scheme connected the reactants to products via the transition states and intermediates. According to Figure 5a, there are the two peaks which represented the transition states and two valleys which represented the intermediates. The activation energy (ΔE) which is the difference between the zero-point energy corrections of the cis isomer and that of the transition states (ts) or intermediates (im) was reported in Table 2, and it also displayed the other characteristics such as the bond length and the dihedral angle.

In this scheme, the hydrogen atom H9 was probably transferred to C10 with the decrease of the force between C9–H9 under high temperature, which increased the bond length of C9–C10, as given in Table 2. A high-energy barrier (294.5 kJ/mol) must be overcome from the ground state (cis 18:1n-9) to the transition state (see ts1 in Figure 4). The attempt to minimize the energy led to the formation of the intermediate (see im1 in Figure 4). Figure 5b showed the vibrational harmonic frequencies calculation, the absence of vibration in 1743 cm^{-1} (C=C stretching vibration, which often multiplied by an appropriate scaling factor because of intrinsic errors from the limitations of the basis set and electron correlation corrections. The scaling factor is 0.9603 for B3LYP/6-31G*.[17]), and the small lengthening of the C9–C10 bond (1.339 Å → 1.408 Å → 1.483 Å) for transition states (ts) and

Table 2. Characteristics of the Cis and Trans Isomers in the Ground States, Transition States (ts), and Intermediates (im) of Scheme as Calculated by the DFT Method

species	activation energy, ΔE (kJ/mol)	bond length (Å)			dihedral angle (deg)
		C8–C9	C9–C10	C10–C11	θ^a
cis 18:1n-9	0	1.506	1.339	1.506	0.409
ts1	294.5	1.507	1.408	1.526	8.769
Im1	278.9	1.478	1.483	1.544	15.440
Im2	267.2	1.478	1.476	1.535	155.640
ts2	286.1	1.509	1.400	1.517	172.883
trans 18:1n-9	−7.6	1.505	1.336	1.505	179.705

^{a}Dihedral angle of C8–C9–C10–C11.

intermediates (im) indicates the conversion of the double bond into a single bond and consequently to the possible rotation of this bond. The appearance of vibration in 2815 cm^{-1} (see st1 and st2 in Figure 5b) may be attributed to the formation of a ring in C9–C10–H9. As the dihedral angle θ (C8–C9–C10-C11) turned by 155.640°, the C9–C10 bond was isomerized to the trans configuration (im2 in Figure 4). According to the data, the energy barrier from one intermediate to another was 11.7 kJ/mol. After another proton transfer (H10 → C9) was finished, the C9–C10 double bond was rebuilt, which led to the formation of trans 18:1n-9.

The proposed scheme can explain the production of the trans isomer reasonably. However, the isomerization mechanism still needs to be discussed. Previous studies have reported that the C–C π bond is essentially broken in the transition state while retaining all σ bonds,[18] and the direct twisting of the C=C double bond causes breakage of the π bond and consequently formation of a diradical product.[19] In the present study, the isomerization of the C=C double bond proceeds via a hydrogen migration pathway without a diradical product. As shown in Table 2, it is concluded that the electrons are delocalized in the C8–C9 and C9–C10 bond in the intermediate which contributes to the very similar bond lengths and stabilizes the structure. The change of bond length of C10–C11 may be attributed to the steric hindrance. To rotate the conformation, π bond is broken in the transition state, and the calculated barriers for the rotation step from one intermediate to another in the scheme is remarkably low (11.7 kJ/mol), which implies that the isomerization reaction may proceed according to this mechanism.

In conclusion, heating treatment induced the formation of trans 18:1 in triolein, and the cis → trans isomerization may occur at 150 °C. Usually cooking/frying food is a relatively short process, and in the present study, the 1 or 3 h treatment is an extreme condition; however, the isomerization is a heat-induced reaction and a cumulative process. This work could not find the formation of trans-fatty acids in a shorter process time under the current analytical techniques. The isomerization of the cis fatty acids, with subsequent conversion to the trans structure, is energetically a more favorable process than the reverse conversion. This conversion then leads to the predominance of trans fatty acids in frying oil. The activation energy of cis and trans isomer of 18:1 calculated by the DFT method indicates the trans isomer possesses a more stable structure and less energy than the cis isomer. According to the production mechanism of trans fatty acids under thermal

treatment, more attention should be paid to the frying process of foods to avoid the risk of TFA intake in the diet.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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