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Formation kinetic study of thermally induced *trans* and conjugated linoleic acids in corn oil

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Background: Corn oil, known for its high linoleic acid (LA) content, is vulnerable to isomerization during thermal processing. This results in the production of harmful *trans*-linoleic acid isomers (TLAs) and small amounts of beneficial conjugated linoleic isomers (CLAs).

Methods: This study examined the change in formation of TLAs and CLAs in corn oil heated to temperatures between 180°C and 240°C, and studied the kinetics of their formation, utilizing infrared spectroscopy and gas chromatography to clarify the reaction's rate-determining steps and underlying mechanisms.

Results: The results indicated the predominant generation of three distinct TLA and CLA isomers, with their levels showing a positive correlation with both the temperature and duration of heating. Importantly, the formation of mono-TLA isomers emerged as the rate-controlling step in the isomerization process, while the presence of O₂ accelerated the formation of both TLA and CLA isomers. This study provided mechanistic insights and predictive models for forming TLA and CLA isomers under aerobic and anaerobic conditions.

Conclusion: These findings imply that modulating the synthesis of mono-TLA isomers could serve as an effective strategy for reducing TLA formation and enhancing the conversion of TLA to CLAs in heated corn oil, thereby establishing a theoretical framework for precisely regulating TLAs.

KEYWORDS

corn oil, linoleic acid, isomerization, kinetics, gas chromatography, infrared spectroscopy

1 Introduction

The World Health Organization (WHO) has endorsed corn oil as a healthy cooking oil. Corn oil comprises approximately 80% unsaturated fatty acids, particularly containing about 49.05% linoleic acid (C18:2-9*c*,12*c*) in its total fatty acid content (He et al., 2017). However, during refining and deep-fat frying, geometric isomerization of linoleic acid in corn oil leads to increased formation of *trans*-linoleic acid isomers (TLAs), primarily C18:2-9*t*,12*t*, C18:2-9*c*,12*t*, and C18:2-9*t*,12*c*. Substantial TLA intake has been linked to an elevated risk of coronary heart disease and various other chronic health disorders (Ganguly and Pierce, 2012; Nestel, 2014; Guo et al., 2023). Simultaneously, position migration of σ bonds in linoleic acid of heated corn oil (He et al., 2017; Nestel, 2014; Guo et al., 2016) generates

trace amounts of conjugated linoleic acid isomers (CLAs), which are beneficial to human health (Guo et al., 2016; Nirvair et al., 2007; Badawy et al., 2023). Therefore, it is crucial to elucidate the underlying relationship between TLA and CLA isomers, develop methods for precise TLA isomer control or efficient TLA-to-CLA isomer conversion, minimize the potential health risks associated with corn oil consumption, and safeguard the nutritional wellbeing of consumers.

Reaction kinetics is a fundamental approach for studying chemical reaction mechanisms by analyzing reaction rates and activation energies to elucidate the relationships between reactants and products. Studies have shown that heating temperature and time significantly affect the formation of TLA and CLA isomers in heated edible oils (Guo et al., 2016). The formation of TLAs isomers increases with temperature and time, and the reaction constants of these isomers exhibit an Arrhenius relationship with temperature (Bialek et al., 2021; Guo et al., 2015). Numerous studies have confirmed the emergence of diverse CLA isomers, including C18:2-9*c*,11*t*, C18:2-10*t*,12*c*, C18:2-9*t*,11*t*, and C18:2-10*t*,12*t*, during heating of edible oils (Guo et al., 2017; Shinn et al., 2017). Our previous research identified C18:2-9*t*,11*t* and C18:2-10*t*,12*t* (*t,t*-CLAs) as the primary CLA isomers in heated triolein. However, the formation mechanisms of these TLA and CLA isomers and their interconversion in corn oil during heating remain unclear and require further investigation (Xie and Xia, 2019; Li et al., 2023).

The complexity of the chemical reactions in heated corn oil stems from the presence of various polyunsaturated fatty acids. When subjected to prolonged or repeated high temperatures, corn oil may undergo processes such as oxidation, isomerization, degradation, and polymerization (Li et al., 2021; Yazdi and Alemzadeh, 2017; Xiang et al., 2024). The isomerization of C18:2-9*c*,12*c* involves an intricate series of interconnected reactions (Aksoy et al., 2021; Chen and Liu, 2020). Consequently, the formation kinetics of the TLA and CLA isomers were investigated to determine the rate-controlling step and optimal heating conditions in both aerobic (O₂) and anaerobic (N₂) environments using infrared spectroscopy and gas chromatography. The findings of this study provide a theoretical framework for effectively controlling TLA isomers in edible oils during everyday cooking practices and optimizing the conversion of TLA isomers to CLA isomers.

2 Materials and methods

2.1 Materials

Corn was sourced from the Yellow River Valley in Shandong, China. Corn oil was extracted and processed by the Xiwang Group through a series of processes, including embryo rolling, pre-pressing, alkaline refining, decolorization, dewaxing, and deodorization. The resulting corn oil met the quality standards for first-class oils specified by the national standard (GB/T 19,111–2017). The average concentrations of TLA and CLA isomers are 1.47×10^{-2} g/g, and 0.23×10^{-2} g/g respectively (He et al., 2017). C18:2 isomer standards were purchased from Sigma-Aldrich (St. Louis, MO). Standards for linoleic acid methyl ester (LAME) mixtures (C18:2-9*c*,11*t*, C18:2-10*t*,12*c*, C18:2-9*t*,11*t*, and C18:2-10*t*,12*t*) were

procured from Matreya (State College, PA, United States). Triundecanoin, used as an internal standard for GC-FID analysis, was obtained from NU-CHEK Prep. Isooctane, used as the chromatographic organic solvent, was obtained from Fisher Scientific (Fair Lawn, NJ). The heating medium consisted of silicone oil (viscosity 500 cSt) procured from the Dingye Industrial Co., Ltd. (Beijing, China).

2.2 Thermal processing

Aliquots of 5 g of each corn oil sample were transferred to a 20-mL micro glass ampoule. The ampoules were either purged with nitrogen gas (N₂) at a flow rate of 5 mL/min for 5 min or left exposed to ambient air and then flame-sealed using an oxy-hydrogen torch. Subsequently, they were subjected to thermal treatments at 180, 210, 220, 230, and 240°C for 6, 12, 18, 36, and 42 h, respectively, in a silicone oil bath (Viscosity 500 Cst, Beijing Dingye Industry and Trade Company). The temperature fluctuations were maintained at $\pm 1^\circ\text{C}$. Upon completion of the designated heating period, the ampoules were extracted from the silicone oil bath and allowed to equilibrate to the ambient temperature prior to further analysis.

2.3 Preparation of fatty acid methyl esters

The corn oil samples were derivatized using the technique described in our previous study (Guo et al., 2017). A 200-mg sample was accurately weighed into a sealed centrifuge tube. The sample was then combined with 2 mL of isooctane containing undecanoic acid triglycerides (serving as an internal standard at 4,000 ppm, equivalent to 8 mg). Subsequently, 0.10 mL of 2 M methanolic potassium hydroxide was introduced. The mixture was vigorously agitated for 30 s, followed by centrifugation at 4,000 revolutions per minute for 10 min. The resulting supernatant was carefully separated, and the upper layer was dehydrated using anhydrous magnesium sulfate.

2.4 Infrared spectroscopy analysis

Corn oil samples were analyzed using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR; Tensor 37, Bruker, Germany). Prior to the sample examination, a background spectrum was acquired within the 400–4,000 cm⁻¹ range. A 5 μL aliquot of each sample was then deposited onto the ATR crystal using a micropipette, followed by 32 scans at 4 cm⁻¹ resolution. Sample analysis was performed immediately after oven removal. Between measurements, the ATR crystal was cleaned with acetone and isooctane. All infrared spectra were recorded in absorption mode. To mitigate issues arising from baseline shifts and peak overlaps, these spectrograms were analyzed in detail (Guo et al., 2017).

2.5 GC-FID analysis

Following methylation, samples were examined using a GC-2010 gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a CP-SIL 88 fused silica capillary column (100 m length, 0.25 mm

diameter, and 0.2 mm film thickness) and a flame ionization detector. The temperature program was initiated at 60°C for 5 min, and then increased to 160°C at 25°C/min. After a 5-min incubation at 160°C, the temperature was further raised at 2°C/min to a final temperature of 220°C and maintained for 25 min. The sample injection volume was 1 mL with a 10:1 split ratio. Nitrogen (99.999%) was used as carrier gas at a flow rate of 6.3 mL/min. The detector flow rates for makeup, hydrogen, and air were set at 30, 40, and 400 mL/min, respectively. Both injector and detector temperatures were maintained at 250°C (Guo et al., 2021). Fatty acids were identified by comparing their retention times with known standards (cis-trans isomers of 2 oleic, 4 linoleic, and 8 linolenic acids), using the calculation method described by Li et al. (2013). Accurate fatty acid concentration measurements were contingent on the absence of intermolecular chemical reactions.

2.6 Formation kinetics of the isomers

Multiple reactions occur during oil heating; however, this study specifically examined the formation rate of isomerization products (TLAs and CLAs) from linoleic acid when heated in O₂ and N₂ environments. The isomer formation rate can be expressed using the following general Equation 1:

$$\frac{d[C]}{dt} = k[C]^n \quad (1)$$

Where C represents the heat-induced isomerization products, *k* denotes the formation rate of isomerization C, and *n* indicates the order of formation with respect to C.

Equation 1 can be integrated over a specified concentration range and time period as shown in Equation 2.

$$\frac{d[C]}{[C]^n} = k dt$$

$$\frac{[C_t]^{1-n} - [C_0]^{1-n}}{1-n} = kt \quad (2)$$

where C₀ and C_t represent the concentrations of C at time 0 and *t*, respectively.

This integral is valid when *n* ≥ 2. For a zero-order reaction, becomes Equation 3,

$$C_t - C_0 = kt \quad (3)$$

When *n* = 1, the result is Equation 4,

$$\ln \frac{C_t}{C_0} = kt \quad (4)$$

In first-order reactions, the rate is proportional to the isomerization concentration in corn oil, and ln (C_t/C₀) is proportional to the reaction duration. In this study, the reaction order was determined using graphical correlations.

The isomerization of C18:2-9c,12c in corn oil to TLA and CLA isomers can be analyzed by examining the relationship between isomer concentration and time. The Arrhenius equation describes the relationship between the reaction rate and temperature Equation 5 is shown below.

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

$$\ln k = \ln A - E_a/RT \quad (5)$$

Where A pre-exponential factor, R is the ideal gas constant, and E_a is the activation energy.

Determining *k* for isomerization at a minimum of three different temperatures allows for E_a calculation from the slope of the plot between ln *k* and 1/*T*.

Using E_a, a mathematical model (Equation 6) relating the isomer concentrations to heating temperature and time can be constructed as follows:

$$[C_t]^{1-n} = (1-n)A \exp(-E_a/RT) + [C_0]^{1-n} \quad (6)$$

This integral was applied for *n* ≥ 2. For zero-order reactions, the mathematical model (Equation 7) is transformed as follows,

$$C_t = A \exp(-E_a/RT) \quad (7)$$

When *n* = 1, the result is

$$t = \frac{\ln C_0 - \ln C_t}{A \exp(-E_a/RT)}$$

namely:

$$C_t = \exp(\ln C_0 - A \exp(-E_a/RT)) \quad (8)$$

2.7 Statistical analysis

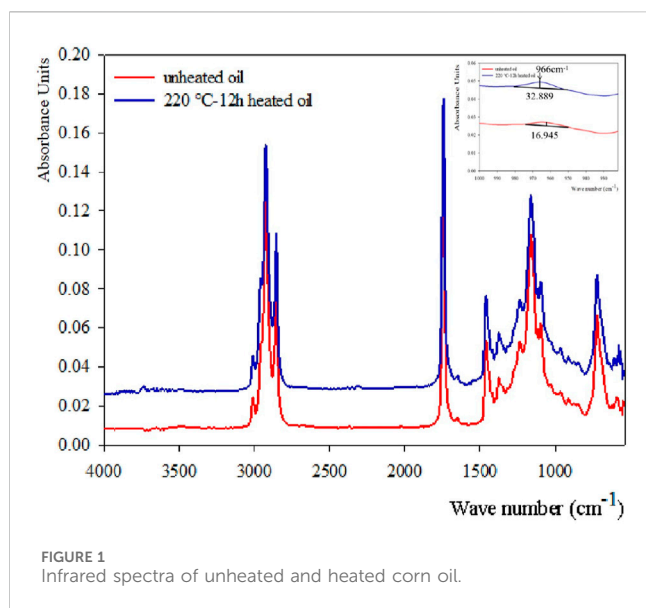
All experiments were performed in triplicate using a completely randomized design. Data visualization was conducted using the SigmaPlot software (version 12.0; Systat Software Inc., San Jose, CA, United States).

3 Results and discussion

3.1 Infrared spectral analysis of TLA and CLA isomers

The infrared spectra of unheated and heated corn oil were analyzed using ATR-FTIR (Figure 1). The spectrum revealed absorption peaks ranging from 3,008 cm⁻¹ to 723 cm⁻¹, indicative of the presence of various functional groups in the corn oil triglyceride components. Notably, the prominent absorption peaks observed at 2,923 cm⁻¹, 2,854 cm⁻¹, 1,743 cm⁻¹, 1,160 cm⁻¹ and 723 cm⁻¹ can be attributed to the symmetric stretching vibration of the hydrocarbon chain, antisymmetric stretching vibration, Fermi vibration of the carbonyl group, C-O stretching bending vibration, and planar rocking vibration of the methylene groups, respectively.

Upon high-temperature heating, significant changes were observed in the corn oil spectra, particularly at 966 cm⁻¹, which represented the C-H groups out-of-plane deformation absorption. Corn oil heated at 220°C for 12 h exhibited a significantly higher absorption at 966 cm⁻¹ (approximately a one-fold increase in peak area) than unheated corn oil (Figure 1), confirming the formation of *trans* fatty acids during high-temperature heating. The intensity of the 966 cm⁻¹ absorption peak in corn oil increased proportionally



with heating time and temperature. The absorption intensity at 966 cm^{-1} was higher in the presence of oxygen (O_2) than in nitrogen (N_2) at the same temperature and heating duration, suggesting that O_2 accelerated the formation of *trans* double bonds. In the presence of O_2 , the *cis* double bond of UFAs undergoes a hydrogen abstraction at the allyl or diallyl position and forms corresponding *cis* double bond radicals, which are thermodynamically unstable, immediately converting into peroxy

radicals ($\text{Rc-O-O}\cdot$) in the subsequent oxidative process to accelerate and induce isomerization reaction. A new finding reported by that Rc-O-O-H is a very important intermediate, and the cleavage of O-O bond (160.97 kJ/mol) in Rc-O-O-H is the rate-controlling step during the *cis/trans* isomerization (Guo et al., 2023). Notably, ATR-FTIR analysis can only detect the total concentration of *trans* fatty acids, and cannot distinguish between mono- and di-*trans* isomers. Christy (2009) demonstrated that linoleic acid can be isomerized to conjugated linoleic acids (CLAs) upon heating at 250°C , with absorption peaks at 987 cm^{-1} and 946 cm^{-1} . However, no corresponding peaks were detected in the ATR-FTIR spectra of corn oil heated at 220°C , implying that the amount of CLAs formed in corn oil under these conditions was likely below the detection threshold of ATR-FTIR.

3.2 GC analysis of TLA and CLA isomers

As shown in Figure 2, the TFA and CLA isomers were observed by heating corn oil under high temperature conditions. The TFAs in corn oil include *trans* oleic acid (C18:1-9t), *trans* linoleic acids (C18:2-9c,12t , C18:2-9t,12c , C18:2-9t,12t), and *trans* linolenic acids (C18:3-9c,12c,15t , C18:3-9c,12t,15c , C18:3-9t,12c,15c , C18:3-9t,12t,15c , and C18:3-9t,12c,15t). The concentration of C18:1-9t increased with both heating temperature and duration. The levels of C18:2-9c,12t and C18:2-9t,12c produced during the heating of corn oil were nearly equivalent and exceeded the amount of C18:2-9t,12t , suggesting that C18:2-9c,12c isomerize more readily to single-*trans* isomers and exhibit a lower tendency to form double-*trans*

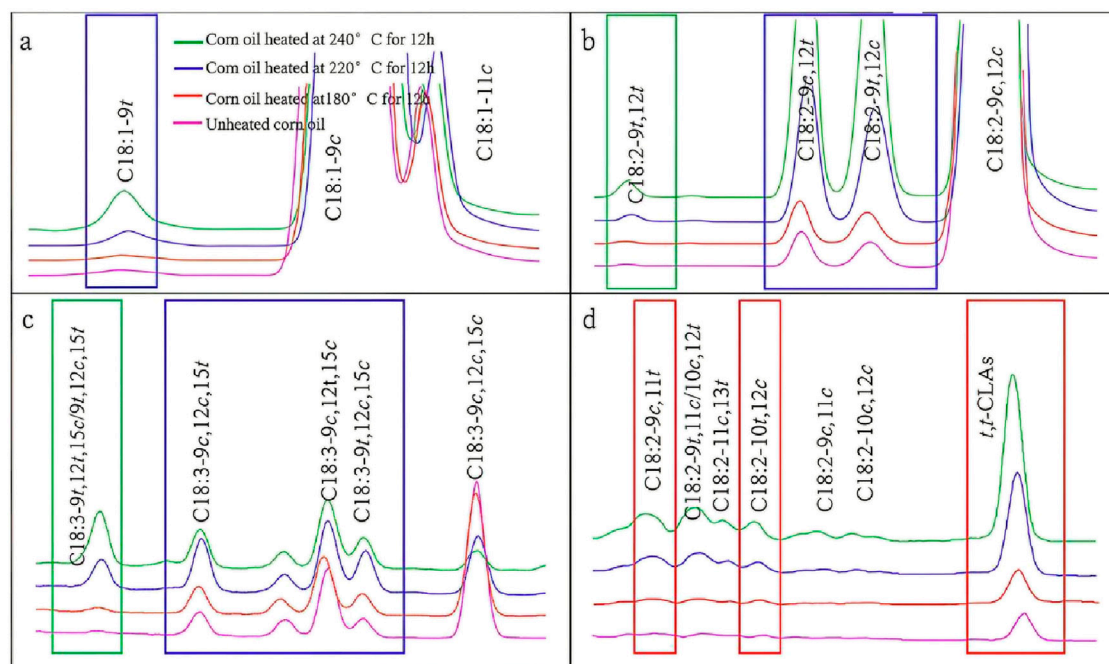


FIGURE 2
(a-d) Gas chromatogram of unheated corn oil heated at 180, 220, and 240°C for 12 h in corn oil.

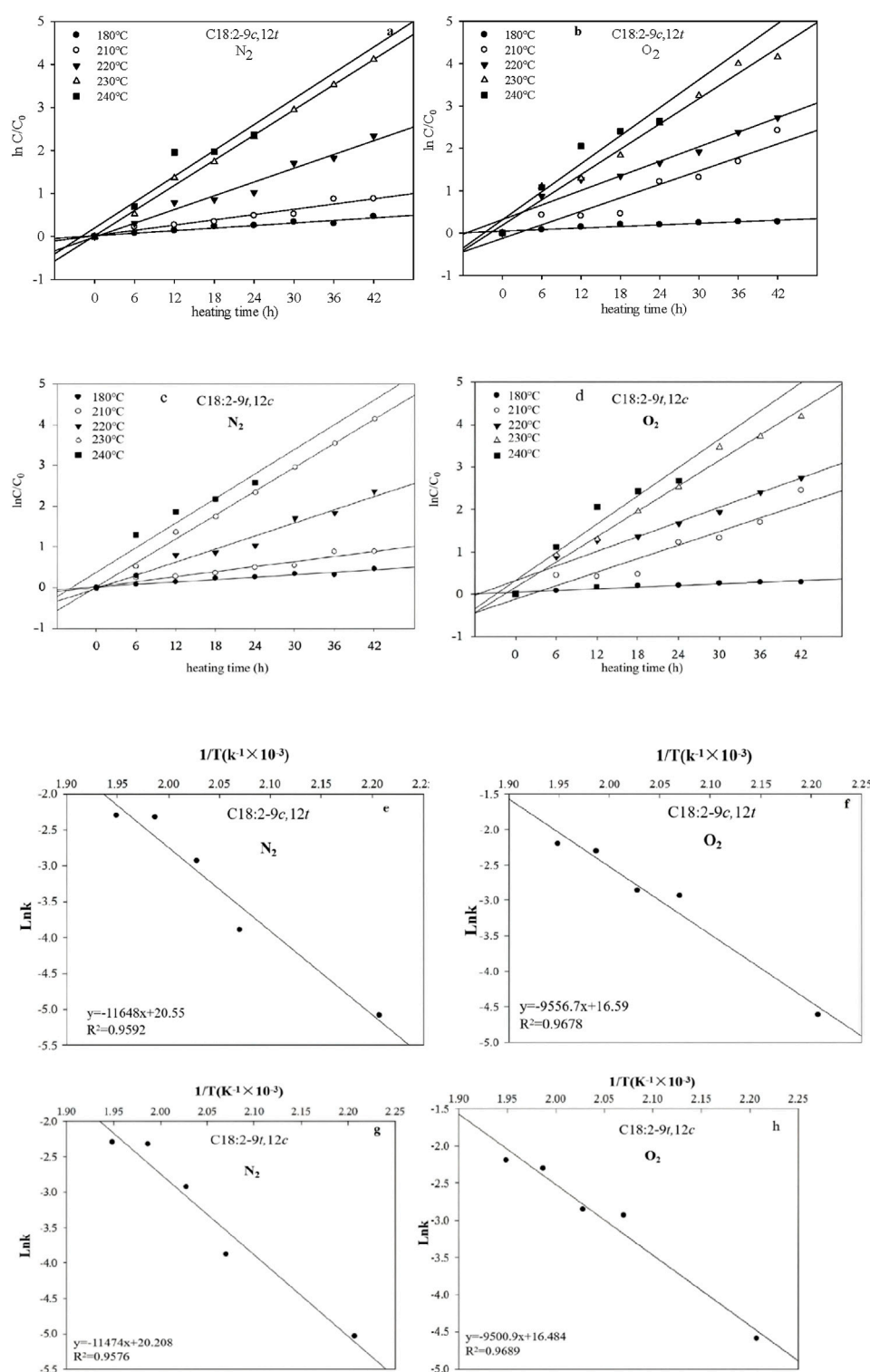


FIGURE 3

Plots showing the correlation between $\ln(C_i/C_0)$ and time for the C18:2-9c,12t in the presence of N₂ (a) and O₂ (b), and the C18:2-9t,12c in the presence of N₂ (c) and O₂ (d), and the relationship between $\ln k$ and $1/T$ for the C18:2-9c,12t in the presence of N₂ (e) and O₂ (f), and the C18:2-9t,12c in the presence of N₂ (g) and O₂ (h) at different temperatures.

isomers under the applied heating conditions. A similar trend was observed in the isomerization of linolenic acid. The concentrations of C18:3-9c,12t,15t, C18:3-9c,12c,15t, and C18:3-9c,12t,15c in corn oil heated for 24 h were significantly lower than those heated for 12 h

at both 220°C and 240°C. This decrease can be attributed to the conversion or degradation of these trans-linolenic acid isomers at higher temperatures and longer heating durations. The above results indicated that the double bonds of UFAs during the heating process

TABLE 1 Kinetic parameters for (1) formation of C18:2-9c,12t; (2) formation of C18:2-9t,12c; (3) formation of C18:2-9t,12t; (4) formation of *t,t*-CLAs; (5) formation of C18:2-9c,11t; and (6) formation of C18:2-10t,12c.

Gas Type	Heating temperature	C18:2-9c,12t		C18:2-9t,12c		C18:2-9t,12t	
	T (°C)	k (h ⁻¹)	E_a (kJ/mol)	k (h ⁻¹)	E_a (kJ/mol)	k (g/100 g) ⁻¹ h ⁻¹	E_a (kJ/mol)
N ₂	180	0.0062	96.8415	0.0065	95.3948	—	59.3013
	210	0.0204		0.0206		0.0065	
	220	0.0534		0.0536		0.0092	
	230	0.0976		0.098		0.0105	
	240	0.1002		0.1007		0.0163	
O ₂	180	0.0099	79.4544	0.0101	78.9905	—	44.4325
	210	0.0531		0.0533		0.0089	
	220	0.0573		0.0577		0.0102	
	230	0.0996		0.0999		0.0118	
	240	0.1103		0.1111		0.0175	
	Heating temperature	t,t-CLAs		C18:2-9c,11t		C18:2-10t,12c	
	T (°C)	k (h ⁻¹)	E_a (kJ/mol)	k (g/100 g) ⁻¹ h ⁻¹	E_a (kJ/mol)	k (g/100 g) ⁻¹ h ⁻¹	E_a (kJ/mol)
N ₂	180	0.0113	62.3484	—	89.6332	—	
	210	0.0234		—		—	
	220	0.0492		0.002		—	
	230	0.0565		0.0028		—	
	240	0.0717		0.0047		—	
O ₂	180	0.0139	61.3498	—	82.9188	—	89.5834
	210	0.0491		0.0015		0.001	
	220	0.0600		0.0025		0.0015	
	230	0.0687		0.0032		0.002	
	240	0.0973		0.0053		0.0039	

first isomerize to give rise to mono-trans isomers, then to double-trans isomers, and finally to multi-trans isomers.

The initial formation of CLAs was characterized by *t,t*-CLAs, indicating a radical-mediated isomerization pathway, followed by the emergence of C18:2-9c,11*t* and C18:2-10*t*,12*c* through extended heating and cooling. As the temperature continued to rise, additional CLA isomers (C18:2-9*t*,11*c*/10*c*,12*t*, C18:2-11*c*,13*t*, C18:2-9*c*,11*c*, and C18:2-10*c*,12*c*) appeared in extremely low amounts (<0.5% total CLA). These findings align with those of previous studies on CLAs isomerization (Li et al., 2013). The diversity and abundance of these isomers increased in response to elevated heating temperatures and prolonged exposure, supporting the results obtained by ATR-FTIR. However, the quantitative analysis of C18:2-9*t*,11*c*/10*c*,12*t*, C18:2-11*c*,13*t*, C18:2-9*c*,11*c*, and C18:2-10*c*,12*c* proved challenging due to their low concentrations.

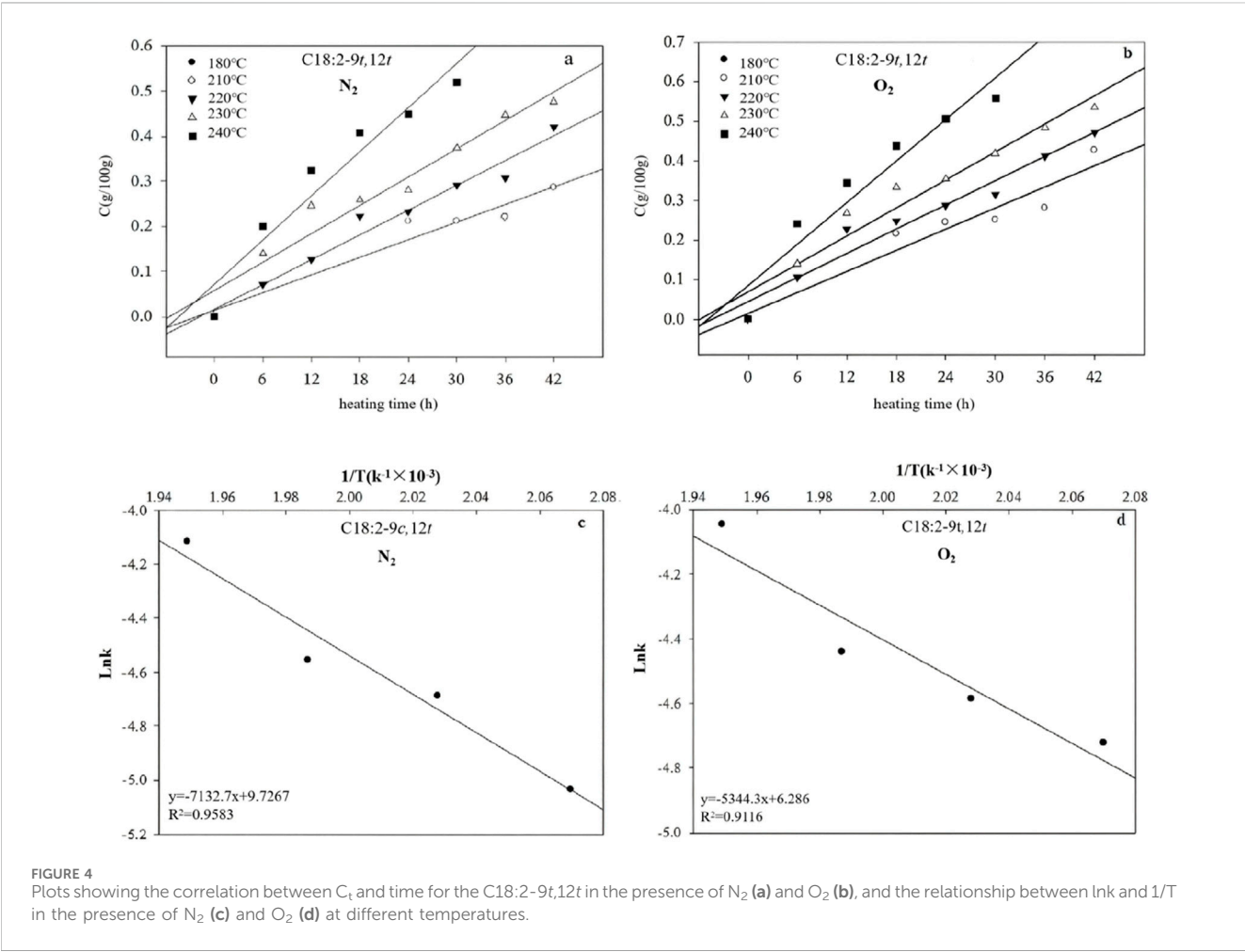
Thus, this study was primarily focused on the formation kinetics of TLAs (C18:2-9*c*,12*t*, C18:2-9*t*,12*c*, and C18:2-9*t*,12*t*) and CLAs (*t,t*-CLAs, C18:2-9*c*,11*t*, and C18:2-10*t*,12*c*) isomerized from linoleic acid in corn oil to further elucidate the mechanisms and key controlling steps of the isomerization process.

3.3 Kinetics for the formation of TLA isomers

The relationships between ln (*C_t/C₀*) and heating duration for C18:2-9*c*,12*t* and C18:2-9*t*,12*c* under N₂ and O₂ atmospheres are shown in Figures 3a,b. The linear correlations observed indicated that the thermally induced isomerization reactions followed first-order kinetics concerning C18:2-9*c*,12*t* and C18:2-9*t*,12*c* concentrations. The rate constants (*k*) derived from the slopes of the first-order plots at 180, 210, 220, 230, and 240°C were

TABLE 2 Dynamic model of heat-induced isomers for concentration, heating temperature, and heating time in the presence of N₂ and O₂.

Heat-induced isomers	Dynamic model-N ₂	Dynamic model-O ₂
C18:2-9c,12t	$C_t = \exp(\ln C_0 - 8.41 \times 10^8 \exp(11.648/T))$	$C_t = \exp(\ln C_0 - 1.60 \times 10^7 \exp(9.557/T))$
C18:2-9t,12c	$C_t = \exp(\ln C_0 - 5.97 \times 10^8 \exp(11.474/T))$	$C_t = \exp(\ln C_0 - 1.44 \times 10^8 \exp(-9.501/T))$
C18:2-9t,12t	$C_t = 1.68 \times 10^4 \exp(7.133/T)$	$C_t = 5.37 \times 10^2 \exp(5.344/T)$
t,t-CLAs	$C_t = \exp(\ln C_0 - 1.48 \times 10^5 \exp(7.499/T))$	$C_t = \exp(\ln C_0 - 1.78 \times 10^5 \exp(7.38/T))$
C18:2-9c,11t	$C_t = 7.39 \times 10^6 \exp(10.781/T)$	$C_t = 1.41 \times 10^6 \exp(9.97/T)$
C18:2-10t,12c	—	$C_t = 4.63 \times 10^6 \exp(10.775/T)$



0.0062 and 0.0065 h⁻¹, 0.0204 and 0.0206 h⁻¹, 0.0534 and 0.0536 h⁻¹, 0.0976 and 0.0980 h⁻¹, and 0.1002 and 0.1007 h⁻¹, respectively, for C18:2-9c,12t and C18:2-9t,12c formation (Table 1). In the presence of O₂, the k values at the same temperatures were 0.0099 and 0.0101 h⁻¹; 0.0531 and 0.0533 h⁻¹; 0.0573 and 0.0577 h⁻¹; 0.0996 and 0.0999 h⁻¹; and 0.1103 and 0.1111 h⁻¹, respectively (Table 1), significantly exceeding those under N₂. These findings suggest comparable formation rates for C18:2-9c,12t and C18:2-9t,12c, which increased with temperature and O₂ presence.

The E_a values for C18:2-9c,12t and C18:2-9t,12c isomer formation were 96.8415 and 95.3948 kJ/mol and 79.4544 kJ/mol under N₂ and 78.9905 kJ/mol under O₂, respectively. These values indicate a reduction in E_a in the presence of O₂ compared with that in N₂. Notably, the E_a values for C18:2-9c,12t were nearly identical to those for C18:2-9t,12c, suggesting that the energy required for thermal formation of C18:2-9c,12t in corn oil was comparable to that of C18:2-9t,12c. By incorporating k and E_a into the first-order kinetic model (Equation 8), the concentrations of C18:2-9c,12t and C18:2-9t,12c isomers in corn oils at various temperatures and heating times were successfully predicted (Table 2).

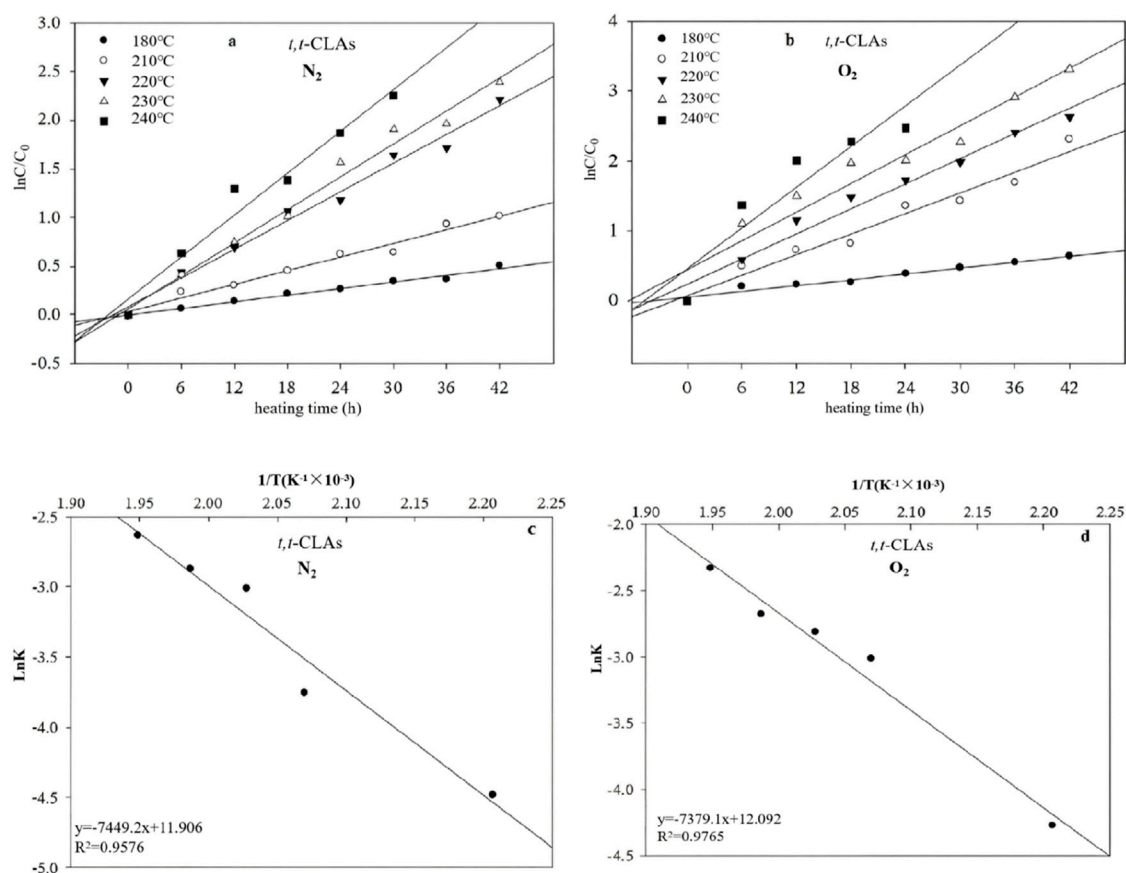


FIGURE 5
Plots showing the correlation between $\ln(C_i/C_0)$ and time for the t,t -CLAs in the presence of N_2 (a) and O_2 (b), and the relationship between $\ln k$ and $1/T$ in the presence of N_2 (c) and O_2 (d) at different temperatures.

At 180°C, C18:2-9*t*,12*t* was not formed in the heated corn oil. It emerged when corn oil was heated to 210°C for 24 h or at 220°C and 230°C for 6 h under N_2 . O_2 presence accelerated C18:2-9*t*,12*t* isomer. Linear correlations between C_i and heating time for C18:2-9*t*,12*t* indicated zeroth-order formation reactions under both N_2 and O_2 (Figure 4). The k values for C18:2-9*t*,12*t* formation increased with increasing temperature under both atmospheres, with higher values observed in O_2 than in N_2 at equivalent temperatures (Figure 4; Table 1).

The activation energy (E_a) for a zeroth-order reaction can be determined using data from a graph correlating $\ln k$ and T^{-1} (Figure 4). The analysis revealed that the E_a values for C18:2-9*t*,12*t* formation were higher in the presence of N_2 (59.3013 kJ/mol) than in the presence of O_2 (44.4325 kJ/mol) (Table 1). This observation indicates that thermodynamic processes will likely dominate C18:2-9*t*,12*t* production. Owing to the superior thermodynamic stability of the t,t conformation relative to the $c,t/t,c$ conformations, the intermediate isomers C18:2-9*c*,12*t* and C18:2-9*t*,12*c* were predominantly transformed into the more stable C18:2-9*t*,12*t*. The reaction temperature primarily influenced these transformations. Furthermore, the zero-order mathematical model (formula 8) was employed, utilizing k and E_a data, to estimate C18:2-9*t*,12*t* isomer concentrations in corn oils subjected to various temperatures and heating durations (Table 2).

3.4 Kinetics for the formation of CLA isomers

Figure 5 shows that the t,t -CLA isomer formation follows a first-order reaction in the heating system in the presence of N_2 and O_2 . Notably, the reaction order remains unchanged with increasing temperature. The k for t,t -CLA formation at 180, 210, 220, 230, and 240°C were 0.0113 and 0.0139 h^{-1} , 0.0234 and 0.0491 h^{-1} , 0.0492 and 0.0600 h^{-1} , 0.0565 and 0.0687 h^{-1} , 0.0717 and 0.0973 h^{-1} , respectively, under N_2 and O_2 atmospheres (Table 1). The k value was higher in the presence of O_2 than in N_2 , indicating that O_2 facilitated the formation of t,t -CLA isomers. Additionally, E_a for the formation of t,t -CLAs was lower in the presence of O_2 (61.3498 kJ/mol) than in N_2 (62.3484 kJ/mol), suggesting that O_2 accelerates the isomerization process. These trends are consistent with the formation of TLA isomers.

In the presence of N_2 , the formation of C18:2-9*c*,11*t* was not observed at 180°C and 210°C and only appeared at 220°C after 18 h. Similarly, C18:2-10*t*,12*c* could not be detected until heating to 220°C for 30 h, rendering its rate constant incalculable. In O_2 , neither C18:2-9*c*,11*t* nor C18:2-10*t*,12*c* were formed at 180°C, emerging at 210°C for 24 h and 30 h, respectively. The concentrations of C18:2-9*c*,11*t*, and C18:2-10*t*,12*c* exhibited linear relationships with heating time and temperature, indicative of zero-order reactions (Figure 6). The k values increased with increasing temperature, and were higher in O_2

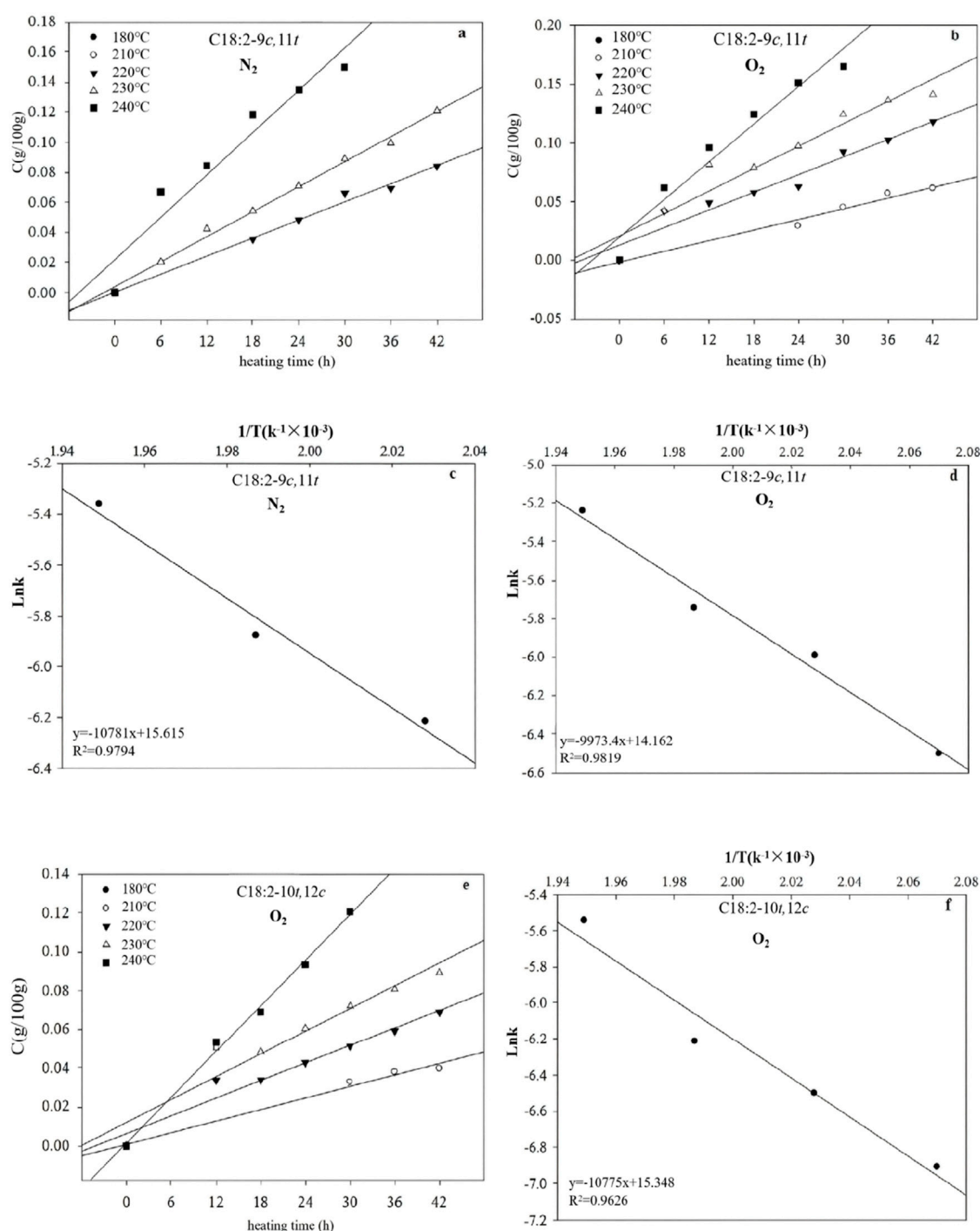


FIGURE 6

Plots showing the correlation between $\ln(C_t/C_0)$ and time for C18:2-9c,11t in the presence of N₂ (a) and O₂ (b), C18:2-10t,12c in the presence (e) of O₂, and the relationship between $\ln k$ and $1/T$ for C18:2-9c,11t in the presence of N₂ (c) and O₂ (d), and C18:2-10t,12c in the presence (f) of O₂ at different temperatures.

than in N₂ (Table 1). Table 1 shows that t,t -CLAs have lower E_a values for isomerization than C18:2-9c,11t and C18:2-10t,12c (Table 1), indicating that t,t -CLAs have lower activation energies for isomerization than C18:2-9c,11t and C18:2-10t,12c. This observation explains why t,t -CLAs are formed first, followed by the generation of C18:2-9c,11t, C18:2-10t,12c, and other isomers. Furthermore, mathematical models relating the concentration,

heating temperature, and time of t,t -CLAs, C18:2-9c,11t, and C18:2-10t,12c were derived (Table 2).

These results demonstrate that linoleic acid in corn oil undergoes isomerization during thermal processing, initially forming equal amounts of mono-TLA isomers, which are then transformed into double-TLA isomers. Concurrently, t,t -CLAs are generated, followed by mono-CLA and *cis*-CLA isomers, as the temperature increases. The

k and E_a values for the formation of mono-TLA isomers were significantly higher than those for double-TLA isomers, suggesting that mono-TLA isomer formation is rate-limiting. Thus, the inhibition of mono-TLA isomer formation can effectively reduce the production of TLAs. For CLAs formation, the t,t -CLAs showed lower k and E_a values than mono-TLA isomers but higher values than double-TLA isomers, suggesting that t,t -CLAs primarily isomerize from mono-TLA isomers and that promoting the conversion of mono-TLA isomers to t,t -CLAs may offer a promising strategy for mitigating TLAs formation. Previous studies showed that the formation of these TFA isomers in plant oil followed the free radical isomerization and proton transfer isomerization mechanisms, via the oxidation-induced isomerization, hydrogen extraction isomerization, direct isomerization, and proton transfer isomerization pathways [4]. These isomerization pathways well explain the formation and distribution of each TFA isomers at different reaction conditions.

4 Conclusion

The UFAs in corn oil undergoes a series of transformations during the thermal processing. It first isomerized to the mono-*trans* isomers, and then isomerized to double-*trans* isomers, finally isomerized to multi-*trans* isomers. This process generates t,t -CLAs, and their associated isomers during the thermal processing. Kinetic analysis revealed that the formation of mono-TLA isomers was the rate-controlling step in the isomerization process, the presence of O_2 accelerated the formation of these TLA and CLA isomers. In addition, the mechanisms and prediction models governing the formation of TLA and CLA isomers in the presence of N_2 and O_2 are elucidated and constructed. These findings suggest that inhibiting the formation of mono-TLA isomers could be an effective strategy to reduce TLAs in heated corn oil, whereas promoting the transformation of TLAs to CLAs offers a promising alternative approach for TLAs mitigation.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

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YH: Writing – original draft. FH: Writing – review and editing. ML: Data curation, Writing – review and editing. ZL: Software, Writing – review and editing. XH: Methodology, Writing – review and editing. HH: Project administration, Writing – review and editing. FG: Project administration, Writing – review and editing. QW: Project administration, Supervision, Writing – review and editing. QG: Funding acquisition, Project administration, Supervision, Validation, Writing – review and editing.

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Conflict of interest

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