Application of Arrhenius Kinetics to Evaluate Oxidative Stability in Vegetable Oils by Isothermal Differential Scanning Calorimetry

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ABSTRACT: In this study, 10 different vegetable oils were oxidized at four different isothermal temperatures (383, 393, 403, and 413 K) in a differential scanning calorimeter (DSC). The protocol involved oxidizing vegetable oils in a DSC cell with oxygen flow. A rapid increase in evolved heat was observed with an exothermic heat flow appearing during initiation of the oxidation reaction. From this resulting exotherm, the onset of oxidation time (T_o) was determined graphically by the DSC instrument. In our experimental data, linear relationships were determined by extrapolation of the log (T_o) against isothermal temperature. The rates of lipid oxidation were highly correlated with temperature. In addition, based on the Arrhenius equation and activated complex theory, reaction rate constants (k), activation energies (E_a), activation enthalpies ($\Delta H^{\ddagger}$), and activation entropies ($\Delta S^{\ddagger}$) for oxidative stability of vegetable oils were calculated. The E_a, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for all vegetable oils ranged from 79 to –104 kJ mol^{-1}, from 76 to –101 kJ mol^{-1}, and from –99 to –20 J K^{-1} mol^{-1}, respectively. Based on the results obtained, differential scanning calorimetry appears to be a useful new instrumental method for kinetic analysis of lipid oxidation in vegetable oil.

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KEY WORDS: Activation energy, differential scanning calorimetry (DSC), enthalpy, entropy, kinetic analysis, oxidative stability, vegetable oils.

Heating is an important part of many food processing operations. Many desirable changes, as well as undesirable reactions, occur in vegetable oils when they are heated at elevated temperature. However, during heating, vegetable oils are very sensitive and susceptible to quality changes, caused by chemical instability, that are dependent on both chemical composition and environmental factors (1,2). Lipid oxidation is one of the major deleterious reactions during heating that markedly affects the quality of vegetable oils (3). This chemical reaction is of primary concern to many researchers in the field of fats and oils. The extensive studies on lipid oxidation have spurred a vast array of findings in the field of fats and oils processing (4–6). Today, it is well known that this deleterious reaction leads to the formation of various oxidation products, which may result in the oil and fat products becoming unfit for human consumption.

Compositional and/or environmental effects on lipid oxidation can be expressed by a mathematical relationship. However, this relationship applies only to several simple food systems and reactions (7). More often, oxidative reactions of vegetable oils are more complex and unique in their behavior, and the appropriate model must be derived individually for each product and oil system. Temperature is one of the main environmental factors that influence the rate of quality loss. The dependence on temperature of most reactions in foods can be expressed more precisely by the Arrhenius model (8).

The oxidation of vegetable oils can be treated as an apparent first-order reaction (7) because of the high concentration of oxygen compared to the amount of oil in the sample. The transfer of an oxygen molecule to an unsaturated fatty acid requires energy. This process can easily be determined by differential scanning calorimetry (DSC) (9,10). DSC is the most widely used thermoanalytical technique for oils and fats. Statistical and mathematical techniques have been applied to DSC data to monitor oxidation of heated oils (2) and to quantify the iodine value (IV) in palm oil (11). Most recently, we used these techniques to determine total polar compounds in heated oils and to characterize various edible oils (12,13).

A good understanding of lipid oxidation kinetics in vegetable oils can improve our abilities to formulate food products that maintain the existing oil quality in a food system and minimize the appearance of undesirable breakdown products. Kinetic data are essential for predicting oxidative stability of vegetable oils under various heat processing, storage, and distribution conditions. Nevertheless, this subject has received very little attention, and kinetic data for lipid oxidation are lacking. This paper presents a comparative study of the oxidative stability of vegetable oils from various plant sources. The main objective of this study was to develop mathematical models to describe the reaction rate as a function of temperature for various vegetable oils. The kinetic data could be used to distinguish the origin of each vegetable oil or to shed some light on the differences or similarities in the oils.

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MATERIALS AND METHODS

Materials and treatments. Vegetable oils (n = 10) from various plant origins were used in this study (canola oil, CaO; coconut oil, CtO; corn oil, CnO; grapeseed oil, GsO; peanut oil, PtO; palm kernel oil, PKO; refined-bleached-deodorized palm olein, $RBDPO_O$; safflower oil, SaO; sesame oil, SeO; soybean oil, SoO). $RBDPO_O$ and PKO were obtained from a local refinery. The other samples were purchased from several local retailers. All chemicals and solvents used were of Analar or high-performance liquid chromatography grade (Merck, Darmstadt, Germany). Fatty acid methyl esters (FAME) were obtained from Sigma Chemical Co. (St. Louis, MO).

Chemical and FAME analyses. AOCS Official Methods were employed to determine free fatty acid content (Ca 5a-40), IV (Cd 1-25), peroxide value (Cd 8b-90), and anisidine value (Cd 18-90) in the oil samples (14). The fatty acid composition of the oil samples was analyzed with gas–liquid chromatography (GLC) after transesterification; the GLC conditions have been reported previously (13).

DSC analysis. The oxidative stability of the vegetable oils was determined by a PerkinElmer DSC-7 (Norwalk, CT). To obtain a baseline, the equipment was calibrated with pure indium in a hermetically sealed aluminum pan. The open aluminum pan was used as the reference. An oil sample of 5.0 ± 0.5 mg was weighed in the open aluminum pan and placed in the equipment's sample chamber. The isothermal temperature was programmed at 383, 393, 403, and 413 K, and purified oxygen (99.8%) was passed through the sample enclosure at 50 mL/min. The onset time (T_o) of the oxidation reaction was taken as the intersection of the extrapolated baseline and the tangent line (leading edge) of the exotherm (Fig. 1, curve B). A kinetic rate constant was taken as the inverse of the onset time ($1 = T_o$, min^{-1}).

Kinetic data analysis. Kinetic data were analyzed following methods adapted from Hill and Grieger-Block (15), Labuza (16), Labuza and Riboh (17), Arabshahi and Lund (18), Cohen and Sagui (19), Haralampu *et al.* (20), and Van Boekel (8). In this study, the effect of temperature on the rate of lipid oxidation was illustrated by means of the Arrhenius equation:

$$\ln (k) = \ln A - E_a/RT \quad [1]$$

where k is the reaction rate constant or reciprocal T_o, A is the pre-exponential factor or frequency factor, E_a is the activation energy (kJ mol^{-1}), R is the molar gas constant (8.314510 J K^{-1} mol^{-1}), and T is the absolute temperature (K). Activation energy and frequency factors were determined from the slopes and intercepts, respectively, of the lines generated by regressing ln (k) vs. $1/T$ by use of a least squares linear regression.

Enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation were determined by regressing ln (k/T) vs. $1/T$ *via* the equation derived from activated complex theory (16):

$$\ln (k/T) = (\ln k_B/h + (S^{\ddagger}/R) - (\Delta H^{\ddagger}/R)(1/T) \quad [2]$$

where k_B is the Boltzmann constant (1.380658×10^{-23} J K^{-1}) and h is Planck's constant ($6.6260755 \times 10^{-34}$ J s). From the slopes and intercepts of the lines, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained.

Statistical analysis. All DSC experiments and measurements were replicated two times. The coefficient of variation for quadruplicate determinations was typically less than 5% for the majority of the DSC analyses employed. All kinetic data were subjected to analysis of variance and regression analyses using the SAS statistical package (21). These procedures were used to fit the least squares linear equations to the kinetic data. Best fit equations were calculated for slopes, intercepts, correlation of determinations (R^2), P-values, and their range of residuals.

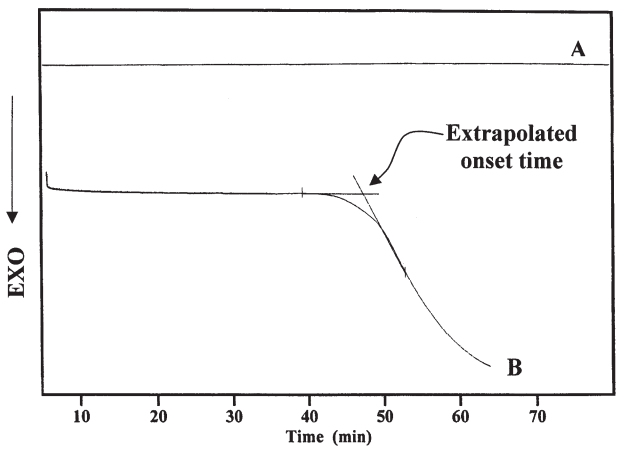

FIG. 1. Differential scanning calorimetric oxidation curve of corn oil. (A) Isothermal curve at 403 K with nitrogen (99.999%) flowed at 50 mL/min; and (B) isothermal curve at 403 K with oxygen (99.8%) flowed at 50 mL/min. Exo, exothermic.

RESULTS AND DISCUSSION

The initial characteristics of vegetable oils used in this study are shown in Table 1. The results indicated that most of the oils were of good quality and that the fatty acid composition of each type of oil was within the range stated in the AOCS Official Methods (14). Lipid oxidation in vegetable oil is primarily an exothermic reaction that produces traces, such as those shown in Figure 1, curve B, during itsothermal DSC experiments. No exothermic peak (i.e., no oxidation reaction) was detected when oil samples were held under nitrogen (Fig. 1, curve A). Figure 2 shows the effect of temperature on the DSC oxidation curves of $RBDPO_O$.

The k values for lipid oxidation of each vegetable oil at each temperature are presented in Table 2. The reaction rate constant was determined for each T from the reciprocal T_o values. On inspection, we see that k alone can be a function of T because the concentration remains constant or nearly so as the temperature changes. Therefore, it is the rate constant that reflects the effect of temperature on the rate of lipid oxidation.

By studying the rates of lipid oxidation as a function of temperature, an increasing rate of oxidation can be observed

TABLE 1
Initial Quality Characteristics of Vegetable Oils Before Differential Scanning Calorimetric Analysis[a]

Oil	Free fatty acid (%)	Iodine value (g of I_2/100 g oil)	Peroxide value (meq/kg oil)	Anisidine value	Fatty acid distribution (%)		
					SFA	MUFA	PUFA
CaO	0.04 ± 0.00	107.84 ± 0.09	6.68 ± 0.01	1.15 ± 0.10	8.9 ± 0.1	63.1 ± 0.1	28.1 ± 0.2
CtO	3.93 ± 0.14	9.37 ± 0.19	1.72 ± 0.04	1.31 ± 0.07	96.0 ± 0.4	3.3 ± 0.2	0.7 ± 0.2
CnO	0.12 ± 0.01	129.01 ± 0.47	3.93 ± 0.01	3.79 ± 0.01	15.9 ± 0.1	27.5 ± 0.2	56.7 ± 0.4
GsO	0.07 ± 0.00	140.58 ± 0.65	10.59 ± 0.31	7.87 ± 0.40	12.5 ± 0.2	18.4 ± 0.1	69.1 ± 0.4
PtO	0.05 ± 0.00	95.23 ± 0.53	6.82 ± 0.06	5.22 ± 0.14	22.5 ± 0.8	50.1 ± 0.2	27.4 ± 0.6
PKO	2.49 ± 0.01	19.30 ± 0.01	0.75 ± 0.09	1.78 ± 0.11	89.7 ± 0.3	8.9 ± 0.3	1.5 ± 0.0
$RBDPO_O$	0.10 ± 0.01	56.55 ± 0.32	0.82 ± 0.06	1.33 ± 0.15	47.6 ± 0.4	42.0 ± 0.3	10.4 ± 0.1
SaO	0.09 ± 0.00	145.38 ± 0.46	5.07 ± 0.15	6.41 ± 0.16	10.4 ± 0.0	13.9 ± 0.2	75.7 ± 0.1
SeO	2.37 ± 0.05	109.24 ± 0.23	1.13 ± 0.08	4.98 ± 0.04	19.1 ± 0.1	40.6 ± 0.1	40.3 ± 0.1
SoO	0.05 ± 0.00	135.70 ± 0.19	2.39 ± 0.09	2.05 ± 0.11	16.9 ± 0.1	23.6 ± 0.1	59.5 ± 0.1

[a]Each value in the table represents the mean ± standard deviation of triplicate analyses. Abbreviations: CaO, canola oil; CtO, coconut oil; CnO, corn oil; GsO, grapeseed oil; PtO, peanut oil; PKO, palm kernel oil; $RBDPO_O$, refined-bleached-deodorized palm olein; SaO, safflower oil; SeO, sesame oil; SoO, soybean oil; SFA, saturated fatty acid; MUFA, monounsaturated fatty acid; PUFA, polyunsaturated fatty acid.

as temperature increases (Table 2). For example, the rates for $RBDPO_O$, PKO, and SoO were 6.3, 7.7, and 6.2 times higher, respectively, at 413 K than at 383 K. At a given T, the rate values were higher in highly unsaturated oils (e.g., GsO, SaO, and SoO) than in vegetable oils with lesser amounts of unsaturated fatty acids (e.g., PKO, CtO, $RBDPO_O$). Generally, oils with higher proportions of unsaturated fatty acids are more prone to oxidation than those containing lesser amounts. However, for sesame oil, a contradictory result was observed. This vegetable oil is known for its high content of unsaturated fatty acids (IV of 109.24 g I_2/100 g of oil); however, its k value was equal to or less than that of vegetable oils containing lesser amounts of unsaturated fatty acids (e.g., PKO). SeO from roasted sesame seeds is known to be resistant to oxidative deterioration (22,23). Its remarkable stability may be caused by the presence of the endogenous antioxidants sesamol and sesaminol, together with tocopherols (24). Another contradictory result was found with the CtO. The IV of CtO in the present study was almost half of that of PKO (Table 1). However, the k value at a given T for CtO was almost 60% faster compared to PKO. This may be caused by the initial high free fatty acid content in CtO. Unbound fatty acids are more prone to oxidation compared to fatty acids bound to the glycerol molecules. We postulate that this may be the main reason for the deviation from the norm for the k values in CtO.

Mathematical models have been used to describe how much faster a reaction will proceed if the product is held at elevated temperature (17). Table 3 provides the regression parameter for the semilogarithmic relationships between k and T in all vegetable oils. As shown in Table 3, the log k values show linear dependencies ($R^2 > 0.96$) on the isothermal temperatures. By using regression equations, the k (and/or T_o) were calculated for a given temperature. These regression equations are useful for predicting oil oxidation at high temperatures during deep-fat frying. As a corollary, this study also predicted the T_o of vegetable oils at 30°C. This parameter may be of interest for predicting the oxidative stability of vegetable oils at room or storage temperature. The T_o values

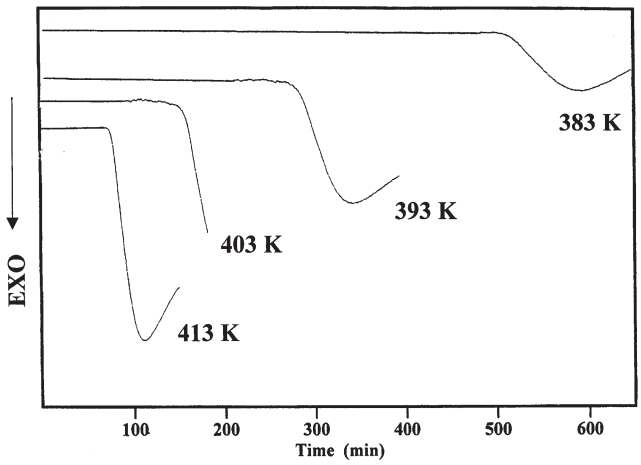

FIG. 2. Differential scanning calorimetric oxidation curve of refined-bleached-deodorized palm olein at 383, 393, 403, and 413 K. Oxygen (99.8%) flowed at 50 mL/min. Exo, exothermic.

TABLE 2
The Reaction Rate Constants (k) at Four Different Temperatures (T) for DSC Oxidative Stability Measurement of Various Vegetable Oils[a]

Oil	Reaction rate constant at different isothermal temperatures, k ($\times 10^3$ min^{-1})			
	383 K	393 K	403 K	413 K
CaO	3.9	7.9	16.2	26.7
CtO	3.1	5.9	11.6	22.3
CnO	6.0	12.0	21.0	46.6
GsO	13.4	27.6	56.8	132.9
PtO	7.9	14.9	25.4	81.8
PKO	1.9	3.7	7.2	14.3
$RBDPO_O$	1.9	3.5	6.2	12.1
SaO	11.3	25.3	55.0	122.3
SeO	1.8	4.0	7.2	14.4
SoO	8.1	15.3	29.7	50.0

[a]Each value in the table represents the mean of four analyses from two replications. For abbreviations, see Table 1.

TABLE 3
Relationship Between log *k* vs. *T* and Predicted T_o Data for Lipid Oxidation of Vegetable Oils[a]

	log *k* vs. temperature (*T*)		
Oil	Regression equation[b]	Correlation of determination, R^2	Reported T_o or "shelf life" at 30°C (d)
CaO	log *k* = 0.0284 *T* –13.2612	0.9934	32
CtO	log *k* = 0.0287 *T* –13.5051	1.0000	45
CnO	log *k* = 0.0291 *T* –13.3855	0.9956	25
GsO	log *k* = 0.0330 *T* –14.5263	0.9983	23
PtO	log *k* = 0.0328 *T* –14.7258	0.9670	41
PKO	log *k* = 0.0295 *T* –14.0493	1.0000	87
$RBDPO_O$	log *k* = 0.0264 *T* –12.8384	0.9988	47
SaO	log *k* = 0.0344 *T* –15.1280	0.9999	35
SeO	log *k* = 0.0293 *T* –13.9555	0.9977	81
SoO	log *k* = 0.0267 *T* –12.3018	0.9974	12

[a]T_o, onset time; for other abbreviations, see Tables 1 and 2.
[b]Significant at $P < 0.0001$.

of vegetable oils at 30°C, as predicted from the regression equations, are also given in Table 3. The reported T_o for highly unsaturated oils (e.g., SoO, SaO, and GsO) was much lower than for oils that contained lesser amounts of unsaturated fatty acids (e.g., $RBDPO_O$, PKO, and CtO).

The basic assumption underlying accelerated shelf-life testing is that the principles of chemical kinetics can be applied to quantify the effects of extrinsic factors such as temperature (as in this study) on the rate of deteriorative reactions. Because the effects of extrinsic factors on deterioration can be quantified, the magnitude of the acceleration can be calculated, and the shelf life of the product under normal conditions determined. However, in most accelerated tests, there are some limitations to the prediction of expected reaction rates at low temperatures. The value of T_o at a lower temperature is subject to a number of additional conditions that may not appear in the accelerated tests. The lipid oxidation at low and high temperatures may go through different steps or reaction pathways depending on the reactivity of metal ions and antioxidants at different temperatures. Moreover, oil temperature affects the degree of oxygen solubility in vegetable oils. The solubility of oxygen decreases by almost 25% for each 10°C rise in temperature (25). Therefore, this results in an underprediction of the T_o at 30°C. The use of pure oxygen (99.8%) also limited our reported T_o values, as they did not represent a real ambient environment. Therefore, the results presented in Table 3 (predicted T_o) are open to considerable uncertainties and errors, and can only be considered as approximate values.

Table 4 provides the regression parameters for Arrhenius relationships between the reaction rate constant and temperature for various vegetable oils. Based on the Arrhenius equation, it is clear that if one plots ln *k* versus 1/*T*, the slope corresponds to the activation energy divided by the molar gas constant. Activation energies for all vegetable oils are presented in Table 5. It can be observed that E_a values for highly unsaturated oils were significantly ($P < 0.05$) higher than those for oils with lesser amounts of unsaturated fatty acids. Even minor changes in E_a values resulted in substantial changes in frequency factors (Eq. 1). A higher activation energy implies that a smaller temperature change is needed to induce a certain change in the rate of oxidation. For example, SaO is more susceptible to oxidative degradation (E_a = 104.26 kJ mol^{-1}) at higher temperature than $RBDPO_O$ (E_a = 79.93 kJ mol^{-1}).

The estimated E_a, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and absolute reaction rates for lipid oxidation in all vegetable oils are summarized in Tables 5 and 6. The high correlation of determination ($R^2 > 0.96$) indicated adequate fit and characterization of the temperature dependence of lipid oxidation by use of activated complex theory. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were greater for highly unsaturated oils (e.g., SaO and GsO) than for oils with lesser amounts of unsaturated fatty acids (e.g., CtO and $RBDPO_O$). The significantly ($P < 0.05$) greater negative $\Delta S^{\ddagger}$ value for $RBDPO_O$ indicates fewer numbers of species in the activated complex state. Hence, the activated complex for lipid oxidation in $RBDPO_O$ is less probable and therefore the rate is slower.

Thus, the temperature dependence of lipid oxidation of vegetable oils can be evaluated by the application of the Arrhenius equation and absolute reaction rates from activated complex theory. The kinetic data gave highly significant ($P < 0.0001$) R^2 for all vegetable oils used. Generally, the isothermal DSC method was successful for investigating oxidative stability of vegetable oils. It should be emphasized that the whole series of experiments and calculations of kinetic data for each vegetable oil can be performed relatively quickly (within one working day). However, fat-containing foods are difficult to test directly using DSC. The feasibility of using DSC to determine oxidative stability of complex food prod-

TABLE 4
Estimated Arrhenius Parameters for Lipid Oxidation of Vegetable Oils (ln *k* vs. 1/*T*)[a]

Regression parameters	CaO	CtO	CnO	GsO	PtO	PKO	$RBDPO_O$	SaO	SeO	SoO
No. of points	4	4	4	4	4	4	4	4	4	4
Slope	–10347	–10450	–10600	–12011	–11923	–10758	–9614	–12539	–10686	–9724
Intercept	21.48	21.48	22.54	27.01	26.17	21.78	18.83	28.24	21.62	20.57
R^2	0.9960	0.9994	0.9935	0.9955	0.9585	0.9994	0.9967	0.9984	0.9982	0.9982
P-value	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Range of residuals	–0.0750 to 0.0715	–0.0240 to 0.0345	–0.1026 to 0.0721	–0.0745 to 0.1003	–0.2627 to 0.2618	–0.0274 to 0.0275	–0.0533 to 0.0636	–0.0462 to 0.0819	–0.0438 to 0.0470	–0.0556 to 0.0447

[a]For abbreviations see Tables 1 and 3.

TABLE 5
Kinetic Constants for Lipid Oxidation of Vegetable Oils[a]

Oil	E_a (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
CaO	86.0 ± 0.4^{c}	82.7 ± 0.4^{c}	−77.0 ± 0.9^{c,d}
CtO	86.9 ± 0.7^{c}	83.6 ± 0.7^{c}	−77.0 ± 1.7^{c,d}
CnO	88.1 ± 0.4^{c}	84.8 ± 0.4^{c}	−68.2 ± 1.0^{c}
GsO	99.9 ± 2.0^{b}	96.6 ± 2.0^{b}	−31.1 ± 5.2^{b}
PtO	99.1 ± 2.8^{b}	95.8 ± 2.8^{b}	−38.0 ± 7.3^{b}
PKO	89.4 ± 0.3^{c}	86.1 ± 0.3^{c}	−74.5 ± 0.7^{c,d}
$RBDPO_O$	79.9 ± 1.2^{d}	76.6 ± 1.2^{d}	−99.1 ± 3.1^{e}
SaO	104.3 ± 3.4^{a}	101.0 ± 3.4^{a}	−20.8 ± 8.8^{a}
SeO	88.8 ± 0.6^{c}	85.6 ± 0.6^{c}	−75.9 ± 1.5^{c,d}
SoO	80.8 ± 2.4^{d}	77.5 ± 2.4^{d}	−84.6 ± 6.2^{d}

[a]Each value in the table represents the mean ± standard deviation of four analyses from two replications. Means within each column with different superscripts are significantly ($P < 0.05$) different. Abbreviations: E_a, activation energy; $\Delta H^{\ddagger}$, enthalpy of formation of the activated complex; $\Delta S^{\ddagger}$, entropy of formation of the activated complex. For other abbreviations see Table 1.

ucts is restricted, mainly owing to the difficulty of obtaining representative samples because of the small sample size (5–15 mg). In the present study, our observations revealed that DSC was an accurate and effective method to investigate the kinetic data of lipid oxidation in vegetable oils at elevated temperature. In conclusion, the isothermal DSC method offers a new way to evaluate the kinetic data of lipid oxidation in vegetable oils owing to its considerable time savings, use of small samples with minimal preparation, and lack of hazardous chemicals.

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TABLE 6
Absolute Reaction Rate Parameters (from activated complex theory) for Lipid Oxidation of Vegetable Oils (ln k/T vs. $1/T$)[a]

Regression parameters	CaO	CtO	CnO	GsO	PtO	PKO	$RBDPO_O$	SaO	SeO	SoO
No. of points	4	4	4	4	4	4	4	4	4	4
Slope	−9950	−10052	−10203	−11614	−11526	−10361	−9216	−12141	−10289	−9326
Intercept	14.50	14.50	15.55	20.02	19.19	14.80	11.84	21.25	14.63	13.5860
R^2	0.9956	0.9994	0.9930	0.9953	0.9559	0.9994	0.9965	0.9983	0.9981	0.9980
p-value	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Residuals range	−0.0753 to 0.0718	−0.0236 to 0.0342	−0.1023 to 0.0717	−0.0742 to 0.0999	−0.2633 to 0.2615	−0.0260 to 0.0272	−0.0530 to 0.0633	−0.0459 to 0.0816	−0.0435 to 0.0473	−0.0559 to 0.0450

[a]For abbreviations see Tables 1 and 4.

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