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DETERMINATION OF OXIDATIVE STABILITY OF EDIBLE VEGETABLE OILS BY PRESSURE DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Rapeseed, soybean, corn and sunflower oils were oxidized in the cell of a pressure differential scanning calorimeter (PDSC). From the resulting PDSC exotherms the characteristic parameters were extracted and used for assessment of the oxidative stabilities of the oils. Sunflower oil appeared to be the least stable. The resistance of the other oils to oxidation depends on temperature. At 110 °C their stabilities are almost the same, but at higher temperatures corn oil is less stable than rapeseed or soybean oil, whereas at lower temperatures this sequence is reversed. As PDSC exotherms were obtained at different temperatures, equations for extrapolation of the PDSC parameters have been proposed and activation energies for oxidation of the oils have been calculated.

INTRODUCTION

The autoxidation of edible oils and fats is one of the reactions leading to their deterioration. As vegetable oils or products of their hydrogenation are widely used in food production, autoxidation is one of the most important problems in storage and processing technology of such food. It is well known that autoxidation of lipids is a chain reaction and can be described by a common set of equations in which RH denotes the lipid molecule

$$\text{Initiator} \xrightarrow{k_0} \text{Products of initiation/radicals I} \tag{1}$$

$$\left.\begin{array}{l} R\cdot + O_2 \xrightarrow{k_1} RO_2\cdot \\ RO_2\cdot + RH \xrightarrow{k_2} ROOH + R\cdot \end{array}\right\} P \qquad \begin{array}{r} (2) \\ (3) \end{array}$$

$$\left.\begin{array}{lll} RO_2\cdot + RO_2\cdot & \xrightarrow{k_3} & \text{Products of recombination} \\ RO_2\cdot + R\cdot & \xrightarrow{k_4} & \text{or disproportionation} \\ R\cdot + R\cdot & \xrightarrow{k_5} & \text{of radicals} \end{array}\right\} T \qquad \begin{array}{r} (4) \\ (5) \\ (6) \end{array}$$

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The letters I, P and T denote initiation, propagation and termination steps, respectively. If the chains are long enough we get

$$\frac{[\mathrm{R}\cdot]}{[\mathrm{RO_2}\cdot]} = \frac{k_2[\mathrm{RH}]}{k_1[\mathrm{O_2}]} \tag{7}$$

and the rate of oxidation can be described as

$$V = \frac{k_1 k_2 [\mathrm{RH}][\mathrm{O_2}]\sqrt{V_0}}{\sqrt{2k_3 k_1^2 [\mathrm{O_2}]^2 + 2\,k_4 k_1 k_2 [\mathrm{O_2}][\mathrm{RH}] + 2k_5 k_2^2 [\mathrm{RH}]^2}} \tag{8}$$

where V_0 is the rate of initiation.

In the limiting case, if

$$k_3 k_1^2 [\mathrm{O_2}]^2 \gg k_4 k_1 k_2 [\mathrm{O_2}][\mathrm{RH}] + k_5 k_2^2 [\mathrm{RH}]^2 \tag{9}$$

which is possible at high partial pressures of oxygen ($p_{\mathrm{O_2}} \gg 13$ kPa) when steps (5) and (6) are neglected, the rate of oxidation can be expressed by a simplified equation

$$V = \frac{k_2}{\sqrt{2k_3}}\sqrt{V_0}\,[\mathrm{RH}] \tag{10}$$

The relationship between eqn. (10) and the susceptibility of a substance to oxidation is evident. The slower the oxidation rate, the more resistant is the substance to oxidation, and vice versa. Consequently, determination of any parameter related to V can be used for ranking the oxidative stabilities of substances.

The oxidation of lipids and other products, both natural and synthetic, according to eqns. (1)–(10) has been under investigation for some years by experimental designs based mainly on analytical methods (determination of peroxide concentrations) or on volumetric methods in which the rate of oxygen consumption is measured. As the oxidation process is exothermic, measurements of enthalpy changes by calorimetry or thermal analysis can be applied for determination of oxidative stabilities. Recent developments in DSC have shown that this technique can be used for autoxidation studies of natural or synthetic products. DSC and its high-pressure modification have been used for oxidation studies of petroleum-based lubricants and fuels [1–6], polyester-based aviation turbine oils [7,8], wood rosins [9] and nitrile rubbers [10]. Thermoanalytical methods have also been used for investigation of edible oils and fats. Cross [11] was the first to use DSC for determination of the oxidative stability of vegetable oils, and he achieved a moderately successful correlation between measurements by DSC and the active oxygen method (AOM). As the DSC transition temperatures were not sharp enough, Hassel [12] has used PDSC as an alternative method to AOM and attained an improved correlation. Dynamic DSC and preliminary isothermal PDSC studies with use of the more popular commercial edible oils have been carried out by Kowalski [13–18]. Raemy and his colleagues from the Nestlé Research Department in Vevey, Switzerland [19] performed normal-pressure DSC studies under isothermal conditions to determine oxidative stabilities of saturated and unsaturated C_{18} fatty acid methyl esters and chicken fat, which served as the model for uninhibited highly unsaturated edible fat. They were able to rank the materials studied, but they reported some difficulty in obtaining measured times for the onset of oxidation. Fatty acid methyl esters and triacyl-glycerols were also studied by dynamic high-pressure DTA [20]. The complex thermoanalytical investigation of rapeseed and sunflower oils has been carried out by means of the Derivatograph [21,22] with the aim of establishing optimum conditions for examining the oxidative stability and oxidation state of oils. The method developed is recommended as being suitable for rapid indication of the oxidative stability of oils under isothermal conditions.

The purpose of this paper was to investigate by PDSC the possible use of experimental parameters for determination of the oxidative stabilities and kinetic features of oxidation of some popular edible vegetable oils, viz., rapeseed (RSO), soybean (SBO), corn (CRNO) and sunflower (SFO).

EXPERIMENTAL

Oils

Vegetable oils were the same as used previously, and their parameters and fatty acid compositions obtained by GLC have been reported elsewhere [13–16].

Apparatus and experiments

A Du Pont 1090 B thermal analyser and a DuPont 990 differential scanning calorimeter equipped with a pressure DSC cell (PDSC, model No. 900830-902) were used. The instrument was calibrated using high-purity indium as standard. Samples of the oils were placed in the open aluminium pan; the masses of samples were in the range 3.5–6.5 mg. Within the designated range, sample weight was not critical. The reference aluminium pan (which was as identical as possible with the sample pans) was left empty. Experiments were performed under 2000 kPa oxygen pressure and oxygen flow was maintained at a level of 100 cm^3 min^{-1}. After preliminary pressurization of the PDSC cell with oxygen to remove air, the pressure, oxygen flow and temperature were adjusted and the experiment was started. Isothermal conditions were chosen to provide reasonable exotherm times. The run data were recorded on 8-in floppy discs and then analysed. From the resulting PDSC heat flow curves the times for the first deviation from

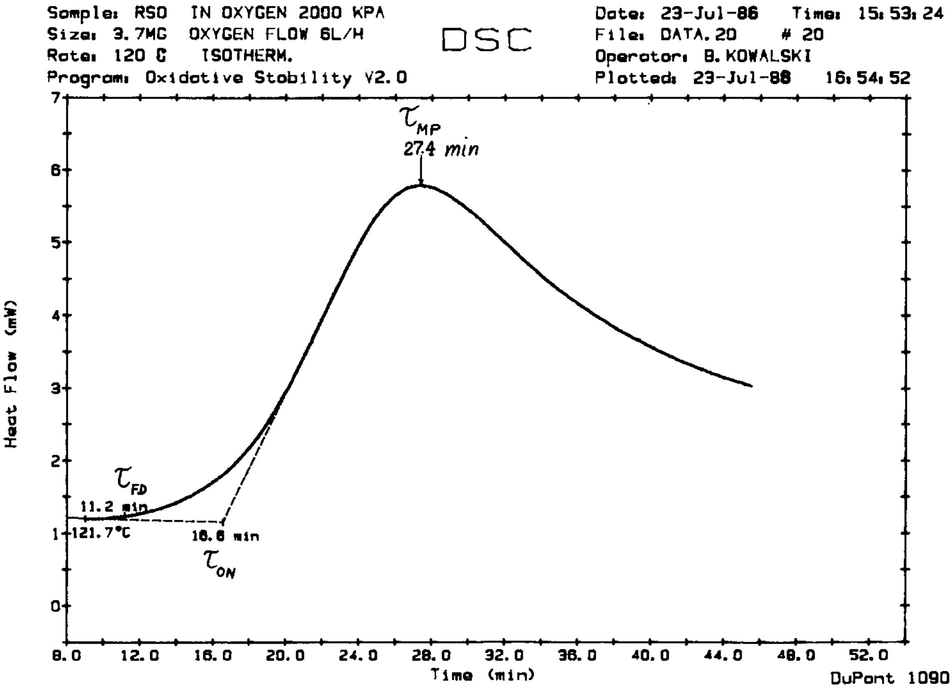

Fig. 1. PDSC exotherm of rapeseed oil at 121.7 ° C. Oxygen pressure, 2000 kPa; oxygen flow, 100 cm^3 min^{-1}.

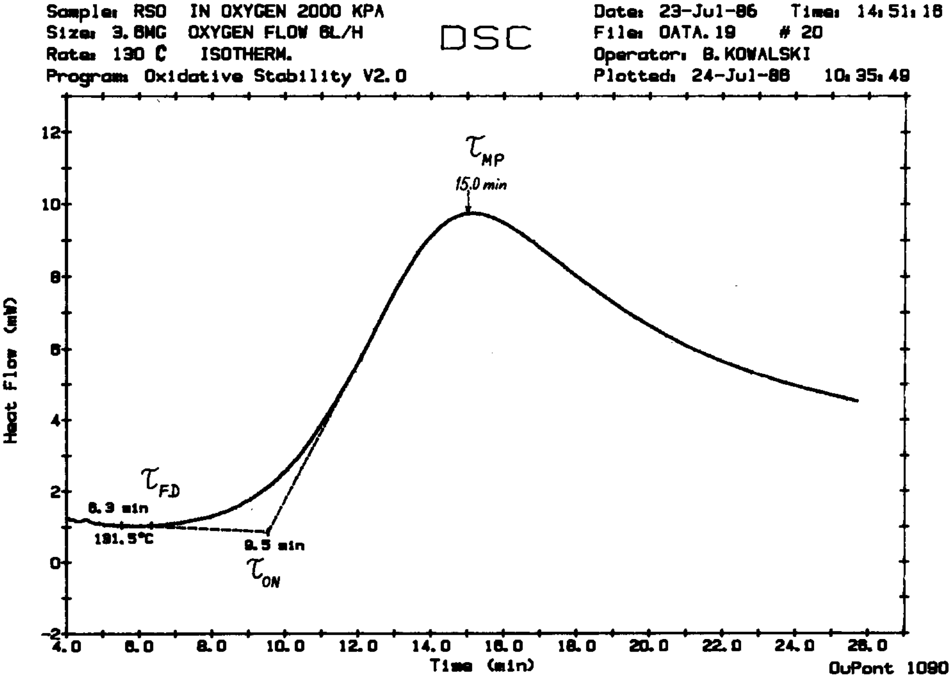

Fig. 2. PDSC exotherm of rapeseed oil at 131.5 ° C. Other conditions as in Fig. 1.

base line τ_{FD}, extrapolated onset of oxidation τ_{ON} and maximum of peak τ_{MP} were determined as shown in Figs. 1 and 2.

RESULTS AND DISCUSSION

The exotherms for the oils studied are shown in Figs. 1–6 and the values of τ_{FD}, τ_{ON} and τ_{MP} are listed in Table 1. The τ_{FD} values showed poor reproducibility, being dependent on the threshold value used in analysis of the data and the thermal history of samples. Similar observations have been reported by Yamazaki et al. in their high-pressure DTA studies [20]. As τ_{MP} and τ_{ON} have shown linear dependence on the reciprocal of exotherm temperatures (Figs. 7–10), the following equations for temperature extrapolation have been proposed

$$\lg \tau_{MP} = AT^{-1} + B \qquad (11a)$$

and

$$\lg \tau_{ON} = aT^{-1} + b \qquad (11b)$$

where A, B, a and b are adjustable coefficients and T is the absolute temperature. The coefficients calculated by simple regression analysis are listed in Table 2.

As $V_\alpha \approx \tau_\alpha^{-1}$, where α is the degree of conversion, based on eqn. (10), τ_α can be used as a measure for determination of the resistance of oils to

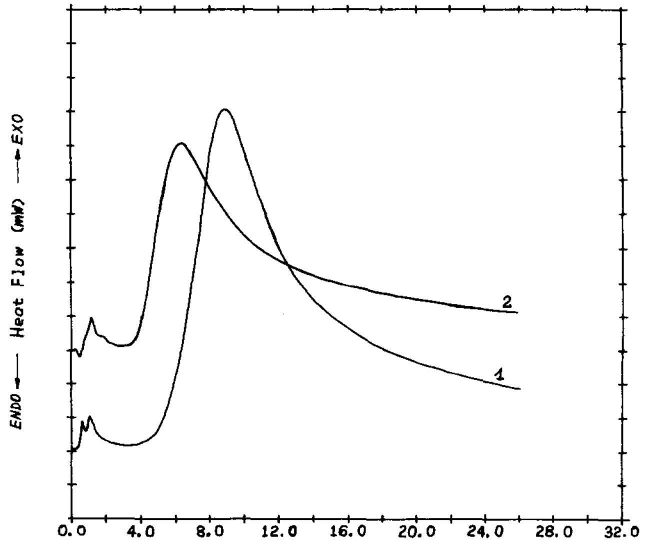

Fig. 3. PDSC exotherms of rapeseed oil in oxygen (pressure = 2000 kPa, flow = 100 cm^3 min^{-1}) at (1) 140.5 °C and (2) 149.5 °C.

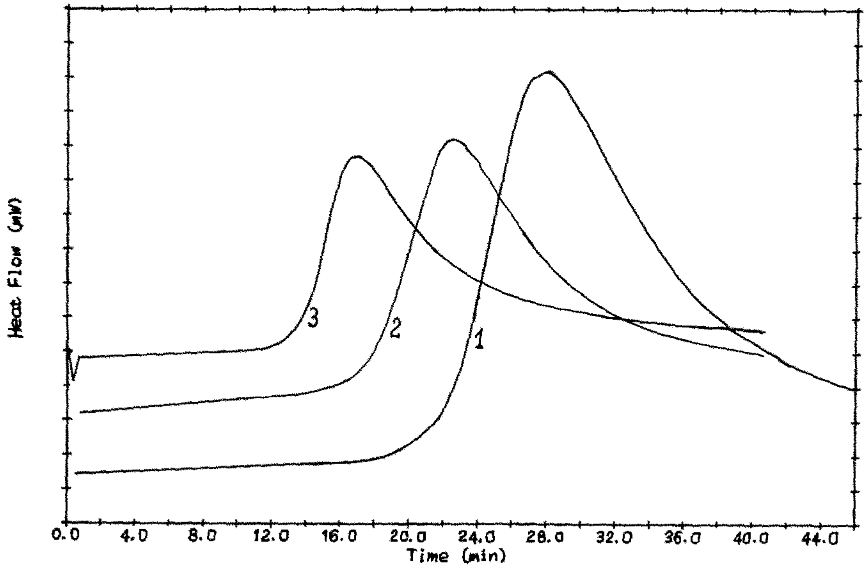

Fig. 4. PDSC exotherms of soybean oil in oxygen (pressure = 2000 kPa, flow = 100 cm^3 min^{-1}) at (1) 121.7 ° C, (2) 126.6 ° C and (3) 131.7 ° C.

oxidation. This resistance is often referred to as oxidative stability. The τ_{MP} values appear to be more consistent than the corresponding τ_{ON} value. Accordingly, the τ_{MP} values were used to rank the oxidative stabilities of the

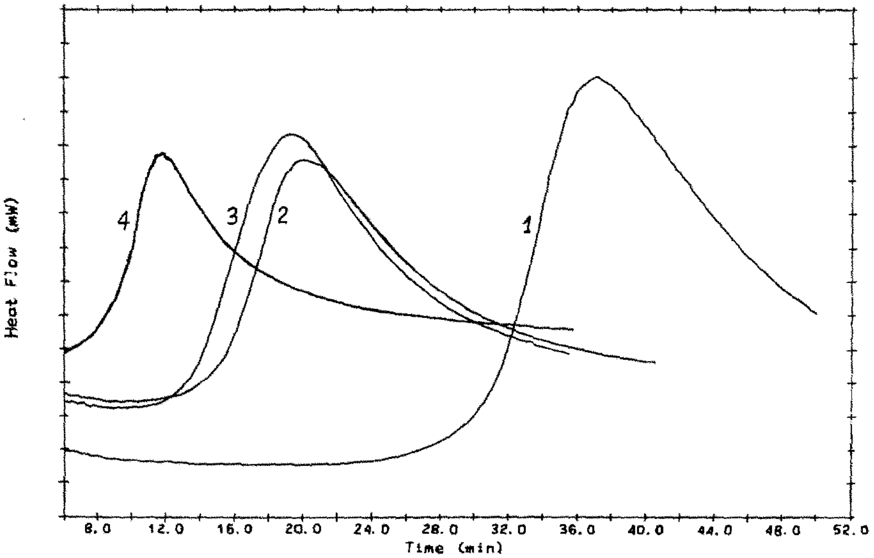

Fig. 5. PDSC exotherms of corn oil in oxygen (pressure = 2000 kPa, flow = 100 cm^3 min^{-1}) at (1) 114.4 ° C, (2) 121.2 ° C, (3) 124.0 ° C and (4) 129.5 ° C.

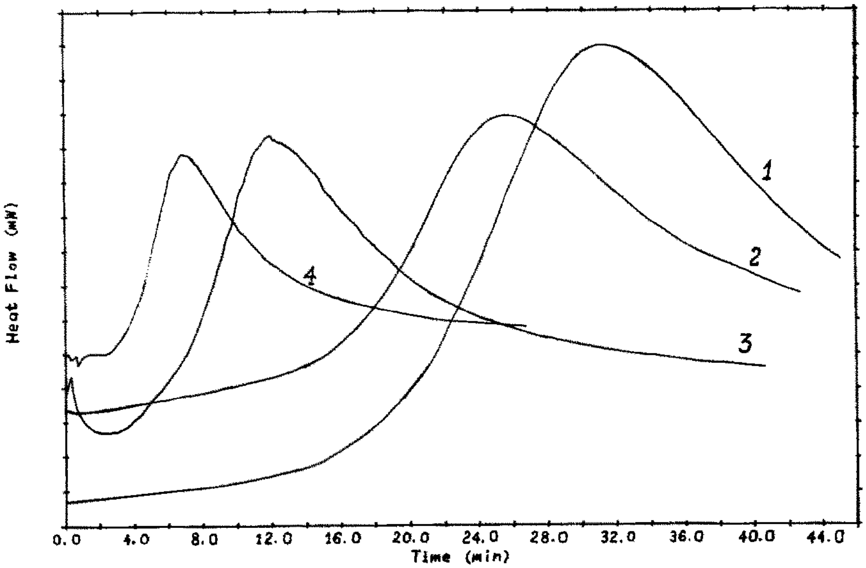

Fig. 6. PDSC exotherms of sunflower oil in oxygen (pressure = 2000 kPa, flow = 100 cm^3 min^{-1}) at (1) 106.2 °C, (2) 111.1 °C, (3) 119.5 °C and (4) 129.2 °C.

TABLE 1

Measured times (τ; min) of PDSC exotherms

Temperature (°C)	τ_{FD}	τ_{ON}	τ_{MP}
Rapeseed oil			
121.7	11.2	16.6	27.4
131.5	6.3	9.5	15.0
140.5	3.5	5.9	9.8
149.5	2.9	3.9	6.3
Soybean oil			
121.7	16.2	22.0	28.0
126.6	11.3	17.7	22.4
131.7	10.4	13.8	16.9
Corn oil			
114.4	23.9	30.5	38.0
121.2	10.5	15.0	20.4
124.0	9.2	13.3	19.4
129.5	3.4	8.2	11.7
Sunflower oil			
106.2	11.9	18.3	31.2
111.1	8.8	13.8	23.5
119.5	3.1	6.3	12.1
129.2	2.5	3.8	6.9

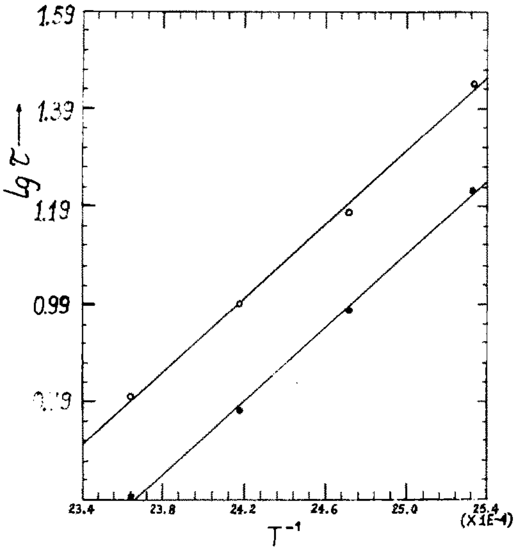

Fig. 7. Lg τ_{MP} (top line) and lg τ_{ON} (bottom line) versus reciprocal temperatures (K^{-1}) of PDSC exotherms of rapeseed oil.

oils. For the oils studied these stabilities decrease in the sequence

CRNO > RSO ⩾ SBO ≫ SFO at $t < 110\,°C$
SBO ⩾ RSO > CRNO ≫ SFO at $t > 110\,°C$

These sequences show that any assessment of the stabilities of oils based on

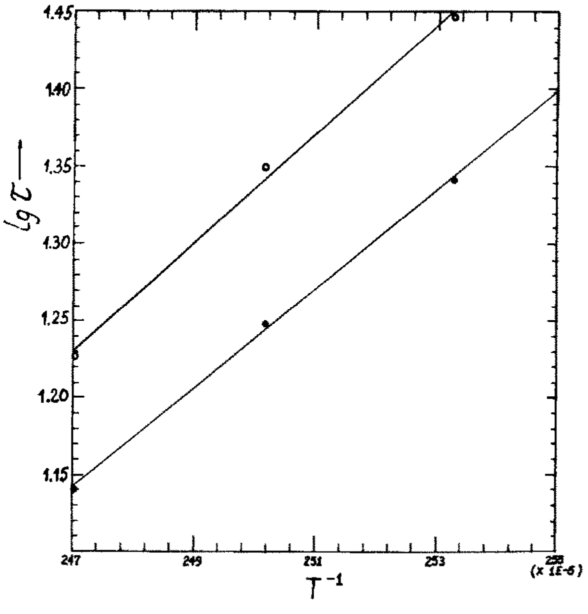

Fig. 8. Plot as in Fig. 7 for soybean oil.

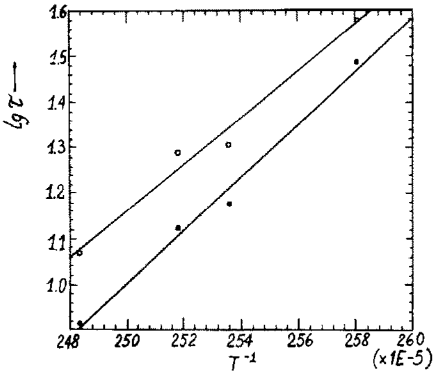

Fig. 9. Plot as in Fig. 7 for corn oil.

a single measurement can be misleading. It should be noted that the experimental results are concerned with the samples studied. From oil technology it is known that commercial oils are usually not 'pure' oils, but rather blends of oils formulated to possess the desired useful parameters. For this reason the results reported here cannot be generalized for a given type of labelled commercial oil.

The CRNO was inhibited against autoxidation by the addition of *t*-butylquinol–citric acid mixture [15,16], and up to 110 °C it was more oxidation resistant not only than the SFO, which had very similar fatty acid composition, but also SBO and RSO. The sequence at $t > 110\,°C$ might suggest that inhibition of CRNO above 110 °C is less effective. It was noted earlier that, for thermal oxidative degradation of CRNO near 220 °C, the above inhibiting system was ineffective [16].The relatively high stabilities of

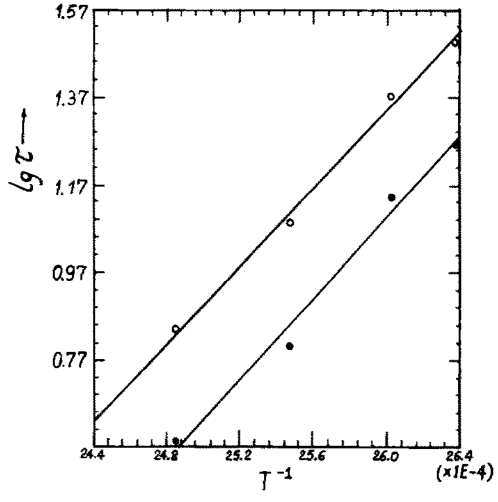

Fig. 10. Plot as in Fig. 7 for sunflower oil.

TABLE 2

Regression analysis of PDSC data and kinetic parameters for oxidation of oils

Parameter	Vegetable oils			
	SBO	RSO	CRNO	SFO
Eqn. (11a)				
A	3509.8 ± 217.5	3755.7 ± 136.2	5147.1 ± 527.7	4420.3 ± 209.0
B	−7.438 ± 0.544	−8.086 ± 0.333	−11.708 ± 1.335	−10.154 ± 0.537
r (correlation coefficient)	0.9981	0.9987	0.9897	0.9978
σ (standard deviation)	0.0096	0.0171	0.0368	0.0241
Equation (11b)				
a	3240.5 ± 111.6	3741.5 ± 99.7	5815.7 ± 425.4	4672.2 ± 389.5
b	−6.863 ± 0.279	−8.263 ± 0.244	−13.536 ± 1.076	−11.051 ± 1.000
r (correlation coefficient)	0.9994	0.9993	0.9947	0.9931
σ (standard deviation)	0.0049	0.0125	0.0297	0.0448
E (kJ mol^{-1})	67.2	71.9	98.6	84.6
lg Z (min^{-1})	7.44	8.09	11.71	10.15

SBO and RSO suggest that these oils possess some natural defence system affording them stability. Probably they contain some natural inhibitors. Inhibitors (antioxidants) of (usually) phenolic or amine type (InH = inhibitor), whether natural or added, would decrease the overall autoxidation rate by the reactions

$$\mathrm{InH} + \mathrm{RO_2}\cdot \rightarrow \mathrm{RO_2H} + \mathrm{In}\cdot \qquad (12)$$

$$\mathrm{In}\cdot + \mathrm{RO_2}\cdot \rightarrow \mathrm{In{-}ROO} \qquad (13)$$

The In· radical is usually stabilized through resonance and there is low probability for promoting a new autoxidation chain.

Propagation and termination steps in the autoxidation scheme of lipids are relatively well recognized, but there is some argument about the initiation step. It can be caused by thermally excited molecules, free radicals either introduced or already present, metal catalysts or light. It has been proved that the most important reaction in initiation is the decomposition of hydroperoxides [23]. Although for kinetic treatment of autoxidation the origin of hydroperoxides is not important, the rôle of direct reaction of oxygen in its singlet state is stressed [24]. The electrophilic reagent $^1O_2$ can react with double bonds of triacylglycerols in 1,4-cycloaddition, ene reaction or 1,2-cycloaddition, giving endoperoxides, allyl hydroperoxides or dioxaethanes, respectively [25]. The compounds thus formed are precursors in initiation of the autoxidation of lipids. Energetically, bimolecular decomposition of hydroperoxides is favoured and the initiation reaction can be described as

$$2\ \mathrm{ROOH} \xrightarrow{k_0} \mathrm{RO_2}\cdot + \mathrm{R}\cdot + \mathrm{H_2O} \qquad (14)$$

If this is so, eqn. (10) can be rearranged into the form

$$V = k_2(k_0/k_3)^{1/2}[\mathrm{ROOH}][\mathrm{RH}] \qquad (15)$$

For long chain-lengths, many hydroperoxide molecules are formed for each free radical initiating the reaction before termination occurs, and hence variations of the overall rate constant k essentially reflect changes in the rate of propagation; i.e., $k_2\sqrt{k_0/k_3} = k = k_2$, and eqn. (15) can be rewritten as

$$V = k_2[\mathrm{ROOH}][\mathrm{RH}] \qquad (16)$$

This is kinetically equivalent to the apparent reaction

$$\text{Oil} + \mathrm{O_2}\ \text{(in excess)} \rightarrow \text{oxidation products} \qquad (17)$$

Equation (16) describes the autocatalytic reaction in terms of substrate and hydroperoxide, and, as is typical for autocatalytic reactions, induction and acceleration periods should be expected. The shapes of PDSC exotherms fit with such a picture. For this autocatalysed reaction, the activation energy E can be determined from the temperature dependence of the time required to reach a constant extent of conversion. The occurrence of the maximum in the PDSC exothermic curve can be utilized to obtain kinetic information by assuming that the extent of conversion at this maximum is constant. Accordingly, the values listed in Table 2 for activation energies and pre-exponential factors Z of the Arrhenius equation for the oils studied were calculated from the coefficients of eqn. (11a).

CONCLUSION

PDSC was used successfully to investigate the oxidative stability of edible vegetable oils. PDSC exotherms allowed ranking of the oils studied and calculation of the kinetic parameters for oxidation of the oils. Although compositions of vegetable oils can vary, both in terms of principal and trace components, and the results obtained here cannot be generalized, the assessment of oxidative stability of oils by PDSC can be performed for any blends of oils, rapidly providing the data for kinetic analysis.

In general, the results obtained in this paper are consistent with established principles of free radical chemistry of lipid oxidation.

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