Technical

Study of the Accelerated Oxidation of Low and High Erucic Rapeseed Oil

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ABSTRACT

The oxidation of a low erucic rapeseed oil was compared to the oxidation of a high erucic rapeseed oil in the temperature range 100 to 140 C. The two oils were found to be very similar in the rate of peroxidation, viscosity increase, change of refractive index, oxidation of the individual fatty acids, and hydroperoxide decay. Rate constants and activation energies for the change of these quantities were determined. The rate of hydroperoxide decomposition was found to be of first order for both oils, but there was evidence that a second order mechanism becomes important at temperatures less than 100 C. Butylated hydroxy anisole (BHA) caused decomposition of hydroperoxide and reacted with fatty acid and possibly with natural antioxidants in the oil. It did not react with oxygen. BHA decomposed thermally between 110 and 140 C. BHA is not an effective antioxidant at these temperatures in an oil which contains esters of highly reactive fatty acids.

INTRODUCTION

Studies of the oxidation characteristics of high erucic rapeseed oil (RSO) have been made (1,2). [Ref. 1 contains a list of most of the practical studies on the oxidation of oils including rapeseed oils.] Recent animal feeding studies (3,4) have shown that it contains harmful substances. The deleterious effects on growing rats, turkeys, and chickens have been attributed to the high erucic acid content. In the past 15 years (5) new strains of RSO have been developed which have only 2 to 4% erucic acid compared with the previous 35 to 40%. The new strains have a very high level of oleic acid and low levels of 20:1 and 22:1 acids. We have carried out a study on both the older high erucic RSO and the new low erucic RSO. (The former has now virtually disappeared from the market.) Both oils were oxidized in the same instrument under the same conditions. It was considered that the two oils could differ in oxidation characteristics and in their ability to be protected by antioxidants. In order to facilitate comparison, activation energies and rate constants were determined for several different physical processes.

EXPERIMENTAL PROCEDURES

Materials

Refined, deodorized, and bleached low erucic and high erucic RSOs were obtained, respectively, from the Pointe Claire Refinery of Procter and Gamble Company of Canada and Monarch Fine Foods, Toronto. Both types of oil were obtained in the summer of 1972. A further supply of low erucic RSO was obtained from Monarch Fine Foods in February 1974. The fatty acid composition of these oils is shown in Table I. Silicone oil was obtained from Dow Corning Silicones International America Limited, Toronto, Ontario. The viscosity of the oil was 0.060 Pascal-seconds (60 cp) at room temperature. Butylated hydroxy anisole (BHA) and butylated hydroxy toluene (BHT) were obtained from DaDon Sales, Mississauga, Ontario, and Fisher Scientific, Toronto, Ontario.

Apparatus

The RSOs were oxidized in 500 ml gas washing bottles (Fisher No. 3-307). The fritted discs at the bottom of the bottles were covered with a ½-in. layer of glass beads to reduce frothing resulting from too small bubble size. Three hundred to three hundred and fifty g of oil were used in each run. The bottles and a 500 watt Vycor glass immersion heater were mounted in a stirred oil bath containing stabilized RSO. The bath was placed inside a polystyrene box; the free space between the bath and the box was tightly packed with glass wool. Total insulation thickness was about 2 in.

The temperature of the oil was measured and controlled by a -80 to 150 C thermistor probe. This was inserted through the bottle cap into a glass tube well to prevent contact of the metal of the probe with the oil under test. The probe was connected through a two way push button switch to a YSI 425C telethermometer and/or a TSI 63RC temperature controller. The latter regulated the current to the heater; an adjustable transformer inserted in the circuit controlled the rate of heating. The temperature readings were compared to those obtained with ASTM mercury thermometers and found to be in substantial agreement. Accuracy of temperature control in the apparatus was ± 0.3 C.

3 L/min of air was supplied from an air pump (Fisher 1-093-5). Moisture and particulate matter were removed by passing the air stream through columns containing silica gel (or anhydrous calcium sulphate) and glass wool.

Fatty acid analysis was conducted on an F & M 810 gas chromatograph. A 6 ft, 20% DEGS on Chrom W 80/100 column was used. The column temperature was 185 C, the injector port 205 C, and the detector temperature 225 C. The flow rate of the helium carrier gas was 75 ml/min and volume injected was 1.2 to 1.7 µl. Refractive indices were

TABLE I

Fatty Acid Content of the Unoxidized High and Low Erucic Acid Rapeseed Oils (RSO) Used in this Study as Determined by Gas Liquid Chromatographic (GLC) Analysis

	16:0	18:0	18:1	18:2	18:3	20:1	22:1
Percent high erucic RSO	3.2	1.3	23.4	17.1	7.8	11.7	35.4
Percent low erucic RSO	4.2	2.6	61.5	15.7	8.9	3.1	4.3

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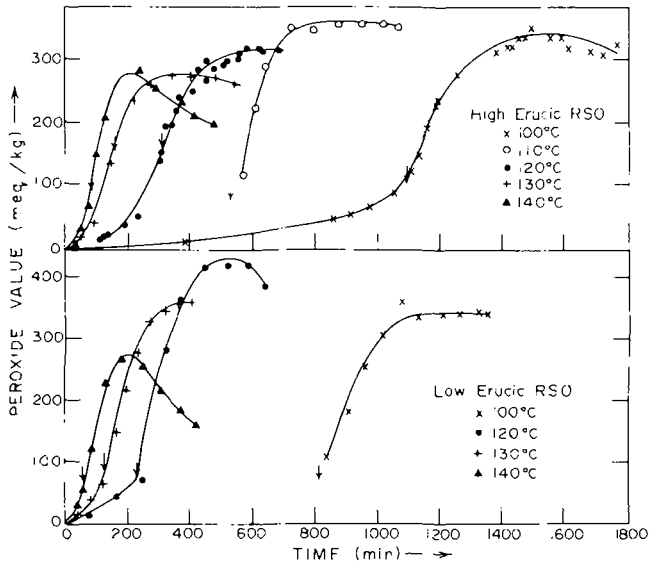


FIG. 1. Peroxide value changes for low and high erucic rapeseed oil (RSO) in the temperature range 100-140 C. The arrows mark the end of the induction period as determined from the refractive index measurements.

determined using a Carl Zeiss Abbe Refractometer. Viscosity of the oils was measured in a capillary rheometer designed and developed in this department. Accuracy was ± 0.5%. Details of the design and operation of this instrument have been published (6).

METHODS

Gas Chromatographic Analysis

The analysis of the fatty acids was carried out using the AOCS official method Ce 2-66 with the following modifications: 7 mg/ml of methyl heptadecanoate was added as an internal standard. Sensitivity factors relative to this were determined for the different methyl esters. All factors were equal to unity within experimental error except that for erucic acid which was 0.931. All analyses were run in duplicate and the concentration of each fatty acid in the oxidized mixtures was calculated using standard procedures.

Oil Oxidation Procedure

It took 30 to 45 min to heat the oil to the experimental temperature. During this period, nitrogen was bubbled through the bottles. Air flow was started once temperature equilibrium was achieved. In the early part of the study two runs were conducted at each temperature in random order. The runs duplicated so well that only one run was considered necessary in the later work. At the lower temperatures, 20 ml aliquots were removed for analysis at 30 min intervals during the autoxidation stage. At the higher temperatures, samples were taken every 10 or 15 min. All samples were stored in opaque bottles at -10 C until analysis could be carried out.

Hydroperoxide Decomposition Studies

The rate of decomposition of hydroperoxides was followed by stopping the reaction at 140 C at, or near, the maximum hydroperoxide concentration and replacing the air percolating through the oil with dry nitrogen. The oil was then cooled to and maintained at the appropriate experimental temperature. Aliquots were removed at regular intervals and the hydroperoxide content determined in duplicate by AOCS official method Cd 8-53.

Viscosity Measurements

Approximately 20 ml of oxidized oil was placed in the small barrel of the rheometer (6) and the temperature adjusted to 20 ± 0.1 C. The viscosity was calculated from triplicate measurements. For some of the more oxidized oils the measurements were made over a range of shear rates to determine the non-Newtonian character of the fluid flow. All reported values are from low shear rate measurements.

BHA Studies

BHA was added to 10 ml of the oil (either RSO or silicone) in a test tube. The tube was heated to dissolve the BHA. The solution was then added to the sample oil which had been preheated to the experimental temperature. The initial concentration of BHA was 0.2%. Aliquots were removed and the BHA concentration was determined using the method of Mahon and Chapman (7).

RESULTS AND DISCUSSION

Changes in Peroxide Value

The changes in peroxide value as oxidation proceeds are shown comparatively in Figure 1 for both high and low erucic RSO. Both oils display the usual features of an induction period which decreases with increase in temperature, followed by a rapid rise in peroxide value during the period of autoxidation. The peroxide concentration then remains at a stationary state level for a considerable period at lower temperatures. The stationary state level is only maintained for a very short period at 140 C.

The peroxide stationary state levels appear to reach a maximum near 110-120 C and drop off at either higher or lower temperatures. The peroxide values at the end of the induction period are 20 to 100 meq/kg. As oils with a peroxide value of 2 meq/kg are considered to be rancid (8), these oils would become rancid long before the end of the induction period at these temperatures. These high induction period values are characteristic of oil containing a considerable amount of linoleic and linolenic acid. The oils contain only natural antioxidant, primarily tocopherols. Tocopherols are reasonably efficient at removing radicals of the type $ROO_2 \cdot$ or $R \cdot$ where these are derived from monounsaturated fatty acids. Abstraction of a hydrogen atom from linoleate or linolenate is, however, more efficient than from tocopherol. Thus considerable hydroperoxide is produced even when an oil contains an optimum amount of tocopherol (9).

Refractive Index and Viscosity Changes

Figure 2 shows that the refractive index increases linearly during the autoxidation stage. The rates of refractive index change which are equal to the slopes of the refractive index curves were found to obey the Arrhenius equation (Fig. 3). The activation energies are recorded in Table II.

The viscosity of the oils rose very rapidly at the completion of the induction period. The high erucic RSO had an initial Newtonian viscosity of 0.069 Pascal-seconds (69 cp), measured at room temperature. At the highest oxidation temperature of 140 C, this increased to 2.9 Pascal-seconds (2,900 cp) after oxidation (including the induction period) for 477 min. The viscosity behavior was non-Newtonian.

Viscosity data for low erucic RSO were obtained only after oxidation at 100 C. The room temperature viscosity of this oxidized oil increased from 0.0788 Pascal-seconds (78.8 cp) to 0.338 Pascal-seconds (338 cp) in 1,360 min or ca. 80% more than high erucic RSO treated under the same conditions.

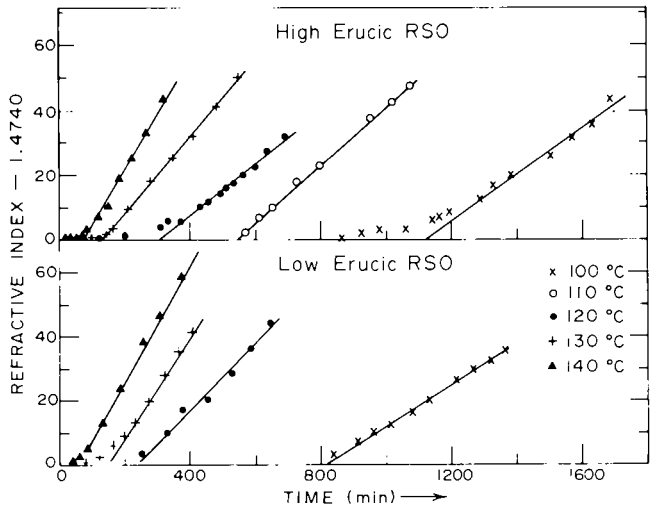


FIG. 2. Refractive index changes for low and high erucic rapeseed oil (RSO) in the temperature range 100-140 C. 1.4740 was the refractive index of the unoxidized oil. The refractive index was measured at 20 C.

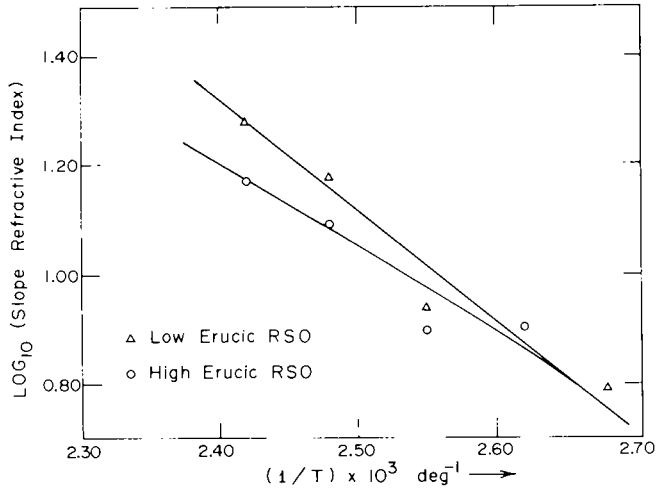


FIG. 3. Arrhenius plot of the rate constants determined from the slope of the refractive index curves shown in Figure 2.

Hess and O'Hare (10) found that the logarithm of the viscosity of the oxidized oil was linearly related to the oxidation time for linseed oil. Figure 4 shows that this is true of the oils studied in this work. The slopes of these curves also obey the Arrhenius equation though the correlation is better with the refractive index plots. (A correlation coefficient of -0.89 was obtained for the viscosity data whereas the refractive index Arrhenius plots had correlation coefficients of -0.99.) Activation energies for the viscosity data are included in Table II as also are the activation energies for other physical changes in the oil.

The refractive index change is seen to be a zero order process whereas the viscosity change is of first order. The difference in order and in activation energy can be partially attributed to the fact that each change is dependent on a different physical process. The viscosity increase involves dimerization and polymerization of molecules and free radicals produced by hydroperoxide and peroxide fission whereas the refractive index change is dependent on conjugation and carbonyl formation in the oil. An R• radical formed in a molecule with two or more nonconjugated double bonds is resonance stabilized. For instance, Swern (11) lists seven resonance hybrids of linolenic acid of which

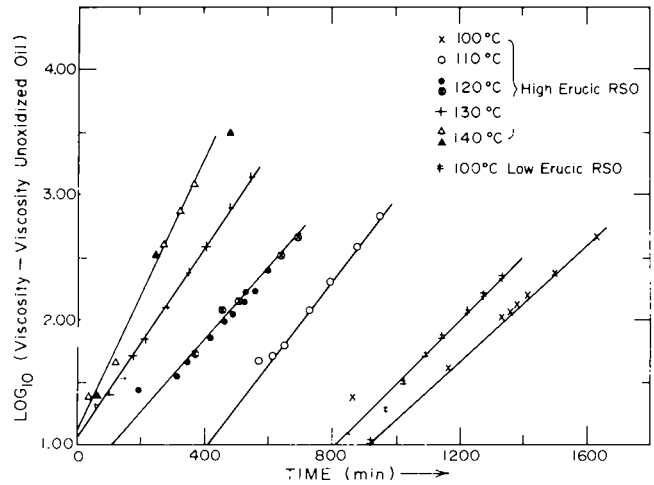


FIG. 4. Plot of logarithm of the viscosity of the oxidized oil minus the viscosity of the unoxidized oil versus time. Some of the curves contain measurements from two different runs. The viscosity of low erucic rapeseed oil (RSO) was only determined at one experimental temperature. All viscosity measurements were conducted at 20 ± 0.1 C.

TABLE II

Activation Energies of the Induction Period, Refractive Index, Viscosity, and Hydroperoxide Decomposition

	Low erucic RSO[a] (kcal/mole)	High erucic RSO (kcal/mole)
Induction period	20 (-0.99)[b]	20 (-0.99)
Refractive index	9.4 (-0.99)	7.1 (-0.99)
Viscosity	---	5.4 (-0.89)
Hydroperoxide decomposition	21	21

[a]RSO = rapeseed oil.

[b]The figures in parentheses are the correlation coefficients of the corresponding Arrhenius plots.

no less than five have two double bonds in conjugation. This should cause an increase in refractive index but the rate of change of the refractive index should decrease in the later stages of oxidation as the conjugated system is very reactive and the molecules containing it should be easily oxidized. Hess and O'Hare (10) have shown from ultraviolet absorption measurements that the rate of formation of conjugated double bonds does decrease corresponding to a viscosity of 1.5 Pascal-seconds (1,500 cp) in linseed oil. This decrease is obviously compensated for by an increase in refractive index-enhancing carbonyl compounds.

The refractive index curves show a sharper change in slope at the end of the induction period than the peroxide value curves. The time corresponding to the juncture of the refractive index curves for the induction period and the autoxidation stage was taken as the end of the induction period. The induction periods are tabulated in Table III as are also the induction periods estimated from the break in the slopes of the peroxide value graphs. The induction periods estimated from the refractive index are marked on the peroxide value curves (Arrows in Fig. 1). This estimate of the induction period appears to be reasonably useful for the low erucic acid RSO and to be adequate at about 100 and 110 C for high erucic RSO. Above this temperature the refractive index measurements appear to overestimate the induction period to the extent that the end of the induction period at 120-140 C estimated from the refractive index is halfway into the autoxidation process for high erucic RSO. This behavior was also found by Hess and O'Hare (10).

TABLE III

Induction Periods for Low and High Erucic Rapeseed Oils (RSO) at Various Temperatures

Temperature (C)	Calculated from change in Refractive Index		Calculated from change in Peroxide Value	
	Low erucic RSO	High erucic RSO	Low erucic RSO	High erucic RSO
	Time (min)		Time (min)	
100	810	1100	860	1120
110	-	535	-	-
120	235	310	250	240
130	135	160	120	100
140	65	90	40	60

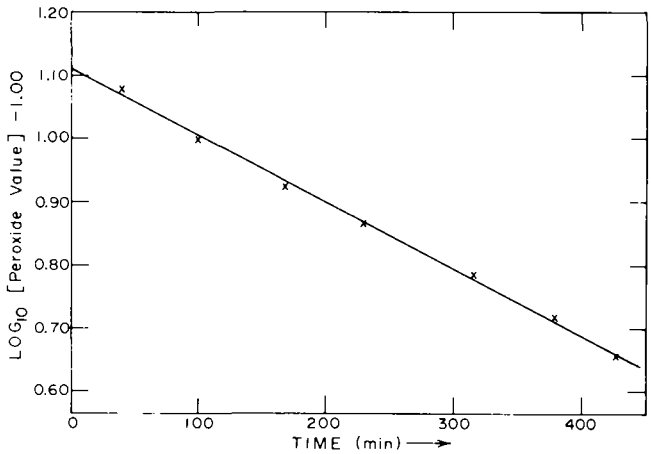


FIG. 5. First order plot of the decomposition of high erucic rapeseed oil (RSO) hydroperoxide at 120 C.

The refractive index measurements are, however, more useful than the viscosity or peroxide results in determining the length of the induction period. The measurement is very easily obtained provided that an accurate Abbe refractometer is used with strict temeprature control.

As the rate of production of peroxy radicals is the first order process, the activation energy of the induction step can be calculated from the slope of the plot of the logarithm of the induction time versus the reciprocal of the temperature. The activation energies obtained for both oils are 20 kcal/mole for the induction process though the induction period for low erucic RSO is 30% less than that for high erucic RSO.

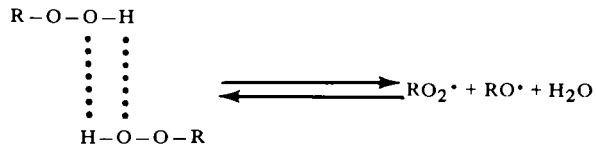
In the activated oxygen method (AOM) the stability of an oil is estimated by determining the time to reach a peroxide value of either 70 or 100 meq/kg at 97.8 C (12). From the measurements obtained in this work it can be seen that this time would correspond approximately to the induction period for these rapeseed oils (1,290 and 1,050 min for high and low erucic RSO respectively). Since there is little or no change in the character of the induction process over the given temperature range, it would appear that a higher temperature than 97.8 C could be used to shorten the time needed to obtain a given AOM value.

Rate of Decomposition of the Hydroperoxides

At temperatures in excess of 110 C, the decomposition of hydroperoxides was found to be of first order (Fig. 5), Table IV. The hydroperoxide decomposition at 100 C of both oils was found by the differential method to have an order of 1.1. At 70 C the order of the hydroperoxide decomposition for low erucic RSO was found to be 1.4.

Most authors (9,13,14) assume that the hydroperoxide decomposition is of first order presumably by analogy with the behavior of most organic molecules. Bolland (15), however, found that the decomposition of hydroperoxides formed from 18 carbon fatty acids or esters was of second order at low temperatures. In a review of his own work, Bateman (16), noted that the decomposition at low temperatures was predominantly of second order but there was a contribution from a first order process also.

Our data are consistent with these findings. At low temperatures, the rate of hydroperoxide destruction is probably of second order with a fairly low activation energy. As the temperature increases, this process becomes less important and the peroxide decomposition is dependent on the higher activation energy of the first order process. Bolland postulated that the second order decomposition occurs through a weak hydrogen bonded complex formed between two hydroperoxides.



The formation of the hydrogen bonds should weaken the O-H and O-O covalent bonds. The rate of the hydroperoxide decomposition would be proportional to the concentration of this complex which in turn is equal to $K(ROOH)^2$ where K is the equilibrium constant for the formation of the hydroperoxide dimer. The temperature dependence of this bimolecular reaction should be strongly

TABLE IV

First Order Rate Constants and Half-Lives for the Decomposition of Hydroperoxide in Low and High Erucic Rapeseed Oil (RSO) in the Temperature Range 100 to 140 C

Temperature (C)	Low erucic RSO k_i $min^{-1} \times 10^4$	Low erucic RSO Half-Life (min)	High erucic RSO k_i $min^{-1} \times 10^4$	High erucic RSO Half-Life (min)
100	0.86	805	0.63	1100
120	3.1	225	2.4	285
130	5.3	130	-	-
140	14.1	50	10.1	70

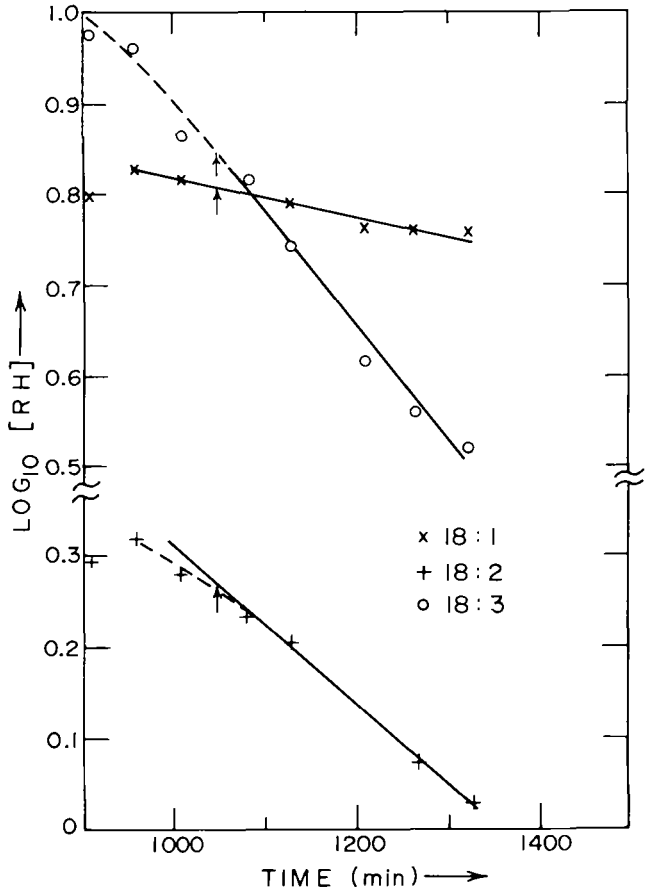


FIG. 6. First order plot of oxidation of the 18 carbon unsaturated fatty acid moieties at 100 C for low erucic rapeseed oil (RSO). The arrows mark the beginning of the stationary state concentration of hydroperoxide in the oxidized oil.

TABLE V

$[k_p/k_t]^{1/2}$ Values for Low and High Erucic Rapeseed Oil (RSO) at 100, 120 and 140 C

$[k_p/k_t]^{1/2} \times 10^4$ (kg/meq/min)$^{1/2}$

Fatty acid	100 C	120 C	140 C
18:1	2.91[a] (2.10)	23 (4.2)	61 (21)
18:2	11.4 (13.4)	87 (28)	134 (95)
18:3	17.4 (17.8)	87 (32)	170 (146)
20:1	5.3 (4.3)	19 (3.6)	33 (28)
22:1	4.5 (7.7)	14 (9.8)	63 (33)

[a]Values not in parentheses are for low erucic RSO, those values in parentheses for high erucic RSO.

influenced by the temperature dependence of K. The activation energy should be close to that of ΔH for the dissociation energy of the hydrogen bonded bimolecular complex, i.e., ca. 10 kcal/mole.

The occurrence of this second order process would appreciably shorten induction periods at low temperatures. For instance, the half-life of the decomposition of low erucic RSO at 70 C can be estimated from the Arrhenius equation for the half-life of a first order process as 12,000 min. The measured half-life is 9,400 min; only 80% as long. This might not, however, have much practical significance at room temperature since oils usually are considered rancid at very low peroxide values.

The linearity of all the activation energy plots shows that in the region 100-140 C only one mechanism occurs. Hess and O'Hare (10) have postulated that there are changes in mechanism which occur at 80 to 100 C and above 130 C. Our finding, that the order of the hydroperoxide decomposition rises as the temperature is lowered, offers some support for this concept of a change in the character of the autoxidation around 80-100 C.

TABLE VI

$k_p/k_t^{1/2}$ Values Relative to 18:1 for Low and High Erucic Rapeseed Oil (RSO) at 100, 120, 140 C

	High erucic RSO			Low erucic RSO		
	18:1	18:2	18:3	18:1	18:2	18:3
100 C	1	6.4	8.5	1	3.9	6.0
120 C	1	6.6	7.5	1	3.1	3.1
140 C	1	4.5	6.9	1	2.2	2.8

Presence of as little as 1 ppm of iron or copper ions can cause fission of hydroperoxide. The oils in this study were analyzed for copper by the extractive method of Persmark and Toregard (17). No copper was detected. The activation energy for the first order hydroperoxide decomposition was 21 kcal/mole for both oils. Though the initiation of oxidation of oil is probably caused by the presence of singlet oxygen (18) the overall reaction is a branching chain reaction resulting from homolytic scission of hydroperoxide. For all intents and purposes this decomposition becomes the effective initiation step even at very low hydroperoxide levels (19). Thus the activation energy obtained for this process should agree with that obtained from the measurement of the temperature dependence of the induction times. From Table II it can be seen that the activation energies estimated by the two approaches agree within the limits of experimental error.

Using the well-accepted chain mechanism for the autoxidation process and assuming that steady state conditions apply, the following equations can be derived.

$$(RO_2\cdot) = \left(\frac{k_i}{k_t}\right)^{1/2} (ROOH)^{1/2} \quad (I)$$

$$-d(RH)/dt = k_p\left[\frac{k_i}{k_t}\right]^{1/2} (ROOH)^{1/2}(RH) \quad (II)$$

$$d(RO_2H)/dt = k_p\left[\frac{k_i}{k_t}\right]^{1/2} [(ROOH)^{1/2}(RH)] - k_i(ROOH) \quad (III)$$

where k_i, k_p, k_t are the rate constants for initiation, propagation, and termination, respectively, and RH, ROOH, and $RO_2\cdot$ denote fatty acid, hydroperoxide, and peroxy radical.

According to the stationary state hypothesis, the $(RO_2\cdot)$ concentration is sensibly constant over most of the reaction period. During the autoxidation stage the hydroperoxide concentration rises by a factor of three to four. From equation (I) we can easily calculate that the $(RO_2\cdot)$ concentration will increase by 70 to 100% in this same stage of oxidation. Thus the use of the stationary state is not justified for the beginning of the rapid autoxidation. At the hydroperoxide maximum the concentrations of all radicals are stationary and the stationary state treatment is justified.

In addition $k_p\left[\frac{k_i}{k_t}\right]^{1/2} (ROOH_{max})^{1/2}$ is constant and the rate of loss of fatty acid becomes a first order process. The changes in the individual fatty acids were determined by analyzing the samples taken during a run by GLC. Data were obtained at 100, 120, and 140 C for both oils. Representative first order plots of logarithm (RH) versus time are shown in Figure 6. It can be seen that the concentrations of fatty acids only begin to decrease at the end of the induction

TABLE VII

Decomposition Rate Constants (First Order) of Butylated Hydroxy Anisole (BHA) in Low Erucic Acid Rapeseed Oil (RSO) and Silicone Oil

Experimental conditions	Temperature (C)	Low erucic RSO k (min^{-1} x 10^3)	Silicone oil k (min^{-1} x 10^3)
N_2 in dark	110	1.2	1.3
N_2 in dark	130	2.1	4.6
O_2 in dark	130	-	4.3
O_2 in light	130	-	7.6

TABLE VIII

First Order Rate Constants of Hydroperoxide Decomposition in Low Erucic Rapeseed Oil (RSO) with (k_0) and without (k_1) Butylated Hydroxy Anisole (BHA)

Temperature (C)	k_0 (min^{-1} x 10^3)	k_1 (min^{-1} x 10^3)	k_1/k_0
110	2.6	5.1	1.8
120	3.6	5.9	1.6
130	6.6	8.9	1.4
140	19.8	38.0	1.8

TABLE IX

Oxidation of Low Erucic Rapeseed Oil (RSO) in the Presence and Absence of Butylated Hydroxy Anisole (BHA) at 130 C

Time of oxidation (min)	Peroxide value with BHA (meq/kg)	Peroxide value without BHA (meq/kg)
0	2.0	2.0
30	18.0	10.0
60	43.0	19.0
75	50.0	29.0
90	57.0	37.0
105	57.0	45.0
120	63.0	64.0
135	68.0	92.0
150	49.0	111
180		

period from values essentially the same as those of the unoxidized oil though hydroperoxide concentration builds up in the induction period. The plots for the very reactive fatty acids are quite linear. More scatter was obtained for the less reactive fatty acids like oleic. Straight lines were fitted to the experimental data in the time regions after the peroxide maximum was obtained. $k_{p,t} = [k_p/k_t]^{1/2}$ was calculated from the equation:

$$k_{p,t} = [k_p/k_t]^{1/2} = \frac{\text{slope x } 2.303}{(k_i \text{ x } ROOH_{max})^{1/2}} \qquad \text{(IV)}$$

The values of $k_{p,t}$ are presented in Table V. Values of this rate parameter relative to that for oleic acid are given in Table VI. k_p ratios near room temperature were found by Bolland (20) to be 1 : (30-40) : (60-80) for oxidation of pure methyl oleate, methyl linoleate, and methyl linolenate, respectively.

At the relatively high temperatures used in this work, the maximum ratio of $k_{p,t}$ for these 18 carbon unsaturated fatty acids is 8.5. The ratios also decrease with increasing temperature. If the reaction between a peroxy radical and a fatty acid molecule involves abstraction of an alpha hydrogen atom, the ratio would be expected to converge to unity with increasing temperature. The activation energy for extraction of a hydrogen atom from linolenate or linoleate would be expected to be (and is) less than that for extraction of an alpha hydrogen atom from oleate, i.e., the higher the activation energy, the greater is the increase of the rate constant over a given temperature interval (20). Thus the oxidation rate for oleate would show a greater increase than that for linolenate or linoleate as the temperature is raised.

Protection of Low Erucic RSO with Butylated Hydroxy Anisole (BHA)

In some preliminary work with 0.005 to 0.02% BHA and butylated hydroxy toluene (BHT), we found that the induction period of the oxidation was unchanged at 120 C compared to the oxidation in the absence of added inhibitor. Some further work was conducted in an attempt to elucidate the reasons for this behavior. According to Pokorny (21) the following reactions may affect the concentration of added antioxidant, AH.

$$AH + ROOH \longrightarrow A^{\bullet} + RO^{\bullet} + H_2O \qquad \text{(V)}$$
$$AH + O_2 \longrightarrow A^{\bullet} + HO_2^{\bullet} \qquad \text{(VI)}$$
$$AH + RO_2^{\bullet} \rightleftharpoons A^{\bullet} + ROOH \qquad \text{(VII)}$$
$$RH + A^{\bullet} \longrightarrow AH + R^{\bullet} \qquad \text{(VIII)}$$

where $A^{\bullet}$ is the free radical generated from the antioxidant.

In addition, thermal decomposition may also cause loss of antioxidant. To investigate these effects, we studied the decomposition of peroxide and BHA in low erucic RSO and the decomposition of BHA alone in inert silicone oil. The BHA concentration used was 0.2%. This high concentration was chosen to allow distinction to be made between the rates of BHA decomposition in the presence and absence of fatty acids and their breakdown products. Only reaction (VI) can occur in the silicone oil.

The first order decomposition constants of BHA in silicone oil and in low erucic RSO are shown in Table VII at 110 C and 130 C. The effect of oxygen and light were determined in silicone at 130 C. Oxygen had little effect but light did enhance the decomposition of BHA. All other oxidations were conducted under an opaque cover. It is noteworthy that the rate of BHA decomposition in the RSO and in silicone are the same at 110 C. They do differ significantly at 130 C. Seemingly, at 130 C reaction (VIII) or possibly the reverse of reaction (VII) are becoming important.

The effect of 0.2% BHA on the decomposition of hydroperoxide was determined in the temperature range 110 to 140 C. Table VIII contains the rate constants in the presence and absence of BHA. The analysis was conducted on the assumption that the rate constant of inhibited decomposition of peroxide is a first order process.

The rate constants of the uninhibited reaction are on the average somewhat higher than our earlier data but the activation energy is the same. (This work was conducted with a sample of low erucic RSO obtained at a later date than that of our earlier work.) From the data in Table VIII, it can be seen that BHA does cause the decomposition of hydroperoxide. At the concentration of BHA used in this work the rate of decomposition was enhanced by ca. 1.6 times.

The effect of BHA on the oxidation of low erucic RSO at 130 C was also determined. The change in the peroxide value in the presence and absence of 0.2% BHA is shown in Table IX. From the peroxide value data it can be seen that the hydroperoxide concentration is much higher in the early stages of the inhibited reaction than the uninhibited, although the final concentration of hydroperoxide in the uninhibited reaction is much higher. This result is consistent with the fact that BHA causes decomposition of hydroperoxide. This enhances the rate of reaction in the early stages of the oxidation as the decomposition of hydroperoxide is the main process of initiation of the

whole reaction. This leads, by the chain effect, to the observed increase in peroxide values. The change in BHA content was also measured. There is no change for the first 30 min of the reaction; thereafter the concentration falls but some 30% of the antioxidant lasts well past the end of the induction period. This type of behavior is not seen when the decomposition of BHA is studied in either silicone or RSO in the absence of air. A possible explanation of this phenomenon is that natural antioxidants present in the oil regenerate BHA and that this protective action falls as these antioxidants are progressively removed.

At this point, we have good evidence that BHA causes the breakdown of hydroperoxide and is itself partially regenerated by the reaction (VIII) where RH is either fatty acid or antioxidant. BHA decomposes with a half-life of 150 min at 130 C. This decomposition, however, is not sufficient to explain the lack of effectiveness of BHA as an antioxidant in this system as a considerable concentration of antioxidant exists well past the normal end of the induction period.

On the other hand, the decomposition of hydroperoxide by BHA is hardly sufficient proof to explain the lack of efficiency of BHA in stabilizing RSO. At a concentration of 0.02% BHA, the rate of peroxide decay would be increased by less than 10%. This does not appear to be sufficient to counterbalance the effect of the antioxidant activity as per reaction (VII) if BHA were an efficient inhibitor at the temperatures employed in these studies. All the evidence seems to point to the conclusion that BHA is not an efficient inhibitor in the temperature range 110-140 C, at least for systems that contain considerable reactive linolenic acid. An effective inhibitor terminates every chain at a chain length close to unity. The high concentrations of hydroperoxide developed in the presence of BHA show that a chain length considerably longer than unity must occur. This is characteristic of an indifferent inhibitor. The peroxide value curve obtained in the presence of BHA is characteristic of a weak antioxidant according to Pokorny (21).

The literature contains conflicting reports about the abilities of antioxidants to stabilize frying fats. Becher and Rost (22) and Sedlacek (23) found that the antioxidants broke down quickly on heating whereas Schmidt-Hebel, Mason, and Rybertt (24) found that BHA and BHT considerably protected linoleic acid in sunflower oil during heating. Probably both results are equally valid. In the absence of reaction (VIII) BHA decomposes rapidly at elevated temperatures. Possibly in sunflower oil there are elements which help to regenerate the antioxidant.

If a natural antioxidant such as tocopherol does regenerate BHA, then this is an example of a process akin to the usual synergism which occurs when two antioxidants used together have a protective value in excess of the sum of their individual contributions. In this case neither antioxidant is particularly effective. Therefore, there is no enhancement of the induction period on addition of BHA.

Changes in viscosity, refractive index, and peroxide value for low and high erucic RSO in the temperature range 100-140 C are very similar. The temperature dependence of each physical property is similar in both oils.

Hydroperoxide decomposition was found to be of first order in the temperature range 100-140 C but the decomposition order was 1.4 at 70 C. It appears that a second order process becomes important at low temperatures.

Linolenic acid is the most easily oxidized acid but the ratio of its rate constant to that of oleic is one-fifth to one-sixth of that found by Bolland (20) for oxidation of the methyl esters of linolenic and oleic below 55 C.

BHA was found to cause the decomposition of hydroperoxide, to react with fatty acids and possibly with natural antioxidants in the oil, but did not react with oxygen. It thermally decomposed at 130 C with a half-life of 150 min. In the temperature range of 110-140 C, BHA does not appear to be an effective antioxidant for rapeseed oil.

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