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ORIGINAL ARTICLE

Modeling the Primary Oxidation in Commercial Fish Oil Preparations

Jenna C. Sullivan · Suzanne M. Budge · Marc St-Onge

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Abstract The quality of commercial fish oil products can be difficult to maintain because of the rapid lipid oxidation attributable to the high number of polyunsaturated fatty acids (PUFA), specifically eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). While it is known that oxidation in fish oil is generally the result of a direct interaction with oxygen and fatty acid radicals, there are very few studies that investigate the oxidation kinetics of fish oil supplements. This study uses hydroperoxides, a primary oxidation product, to model the oxidation kinetics of two commercially available fish oil supplements with different EPA and DHA contents. Pseudo first order kinetics were assumed, and rate constants were determined for temperatures between 4 and 60 °C. This data was fit to the Arrhenius model, and activation energies (E_a) were determined for each sample. Both E_a agreed with values found in the literature, with the lower PUFA sample having a lower E_a. The oil with a lower PUFA content fit the first-order kinetics model at temperatures ≥20 °C and ≤40 °C, while the higher PUFA oil demonstrated first-order kinetics at temperatures ≥4 °C and ≤40 °C. When the temperature was raised to 60 °C, the model no longer applied. This indicates that accelerated testing of fish oil should be conducted at temperatures ≤40 °C.

Keywords Lipid chemistry · General area, lipid hydroperoxides · Oxidized lipids, fish oil · Specific lipids

J. C. Sullivan (✉) · S. M. Budge
Department of Process Engineering and Applied Science, Dalhousie University, Halifax, NS B3J 2X4, Canada
e-mail: jcsulliv@dal.ca

M. St-Onge
Ascenta Health Ltd., 4-15 Garland Avenue, Dartmouth, NS B3B 0A6, Canada

Introduction

Fish oil dietary supplements have been gaining popularity in recent years due to the health benefits provided by the polyunsaturated fatty acids (PUFA) they contain. The primary PUFA in fish oil are eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). These fatty acids (FA) have been shown to be important factors in cardiovascular health as well as brain and eye development in babies [1–6] while deficiencies in PUFA have been associated with a number of negative health conditions including dermal conditions, attention deficit disorder and clinical depression [4]. Because most people do not consume the recommended 2–3 servings of fatty fish per week as recommended by the World Health Organization [7], fish oil supplements have become a popular alternative. Unfortunately, due to their large number of double bonds, PUFA in fish oil are subject to rapid oxidation which produces fishy off-flavors and can make supplements unpalatable.

The type of oxidation most commonly seen in commercial fish oil products is a result of direct interactions between fatty acid radicals and molecular oxygen. This process is initiated by reaction of singlet oxygen with lipids [8] to generate free radicals that in turn, initiate chain reactions of oxidation. Oxidation of PUFA leads to the formation of the primary oxidation products, lipid hydroperoxides, which then break down into secondary oxidation products including aldehydes, ketones, acids, and alcohols. Hydroperoxides are stable at room temperature, but readily decompose at elevated temperatures or in the presence of transition metals [9]. The rate of formation and degradation of hydroperoxides increases with increasing temperature [10]. Hydroperoxides are an important measure of oil quality as they are an indicator of the future levels of secondary oxidation products that negatively impact sensory

parameters. There are a variety of other factors, including fatty acid composition, lipid class composition, concentrations, and type of oxygen present, antioxidants and light, that can influence oxidation, and make accurate comparisons between oxidation studies difficult [9].

Tests of oxidative stability are commonly used to evaluate the shelf life of fish oils, but in order to complete testing in a reasonable amount of time, elevated temperature is frequently used to accelerate oxidation. The goal of this accelerated testing is to obtain results that can then be used to predict the shelf life of fish oil products that are stored under normal conditions [11]. For this to be possible, the kinetics of the oxidation reaction must be determined. Theoretically, oxidation rates can be monitored by following the degradation of specific FA. Though this has been attempted in fish oils [12], these oils have a complex FA profile and application of these techniques may not give an accurate representation of oxidation that is occurring in the oil as a whole. At normal oil storage temperatures the change in fatty acid profile happens very gradually and fatty acid analysis may not be sensitive enough to detect the minute changes in fatty acid concentration, making this method impractical to use for monitoring oxidation of fish oils. Rather than monitoring fatty acid composition of fish oils, other studies use oxygen concentrations to assess oxidation [e.g. 13, 14], a technique that may be more accurate for fish oil oxidation though it does not directly take into account the formation of oxidation products that could impart negative flavors into the oil. No studies could be found that attempt to decipher the kinetics of fish oil oxidation using a common oxidation indicator. The present study uses peroxide values (PV) to assess oxidation because these compounds are formed directly from lipids and therefore, the amount of hydroperoxides present can be directly related to the amount of oxidized lipid present at early stages of oxidation.

This study evaluates the stability of two commercially available liquid fish oil supplements for oxidative stability by monitoring hydroperoxide formation at a number of different temperatures, ranging from 4 °C to 60 °C to determine if oxidation of fish oil follows the Arrhenius model. This information is important to fish oil manufacturers as it will enable the application of accelerated stability data to real-time conditions, thereby reducing the time required to perform stability studies from years to weeks.

Experimental Procedures

Materials

Two different types of commercially available liquid fish oil supplements were obtained from a retail outlet. The first was NutraSea, a typical "18:12" fish oil, containing approximately 18% EPA and 12% DHA as proportions of total FA. The second was NutraSea HP, a fish oil "concentrate" containing approximately 30% EPA and 10% DHA. Both products were produced by Ascenta Health and contained winterized fish oil (97.86%), natural flavor (2%), alpha tocopherol (0.04%) and green tea catechins (0.1%). Amber bottles (200 ml) and lids were supplied by Ascenta Health. These products were marketed as fish oils and contained triacylglycerols (TAG) as the primary lipid at 70–75%. Monoacylglycerides (MAG) and diacylglycerides (DAG) were also preset at 20–25% and <5%, respectively.

Potassium iodide, 1% starch indicator, sodium chloride, butyl hydroxytoluene, boron trichloride-methanol, anhydrous sodium sulfate, Optima acetic acid and Optima isooctane were obtained from Fisher Scientific (Ottawa, ON). Optima chloroform was obtained from VWR (Mississauga, ON). An Isotemp 100 Series Model 126G oven (Fisher Scientific) was used to incubate samples. Methyl tricosenoate, methyl eicosapentaenoate, and methyl docosahexaenoate were obtained from Nu-Chek Prep (Elysian, MN).

Methods

Fatty Acid Analysis

Both fish oils were analyzed for EPA and DHA via GC-FID. Triacylglycerols were converted to methyl esters (ME) following the modified Global Organization for EPA and DHA Voluntary Monograph for Omega-3 [15], using methyl tricosenoate as an internal standard, as well as external standards for EPA and DHA. ME were separated using a column coated with (50% cyanopropyl)-methylpolysiloxane (30 m × 0.25 mm × 0.25 μm film thickness) and helium was used as the carrier gas at a flow rate of 1.0 ml/min. The oven temperature was initially held for 2 min at 153 °C then increased at 2.3 °C/min to 205 °C and held for 8.3 min. The total run time was approximately 32 min. The FID was maintained at 270 °C, and the injector (split mode 1:100, 4 mm liner) at 250 °C.

Stability Studies

Both oils were incubated in the dark at 4, 20, 40, and 60 °C. The 18:12 oil was also incubated at 30 °C. Three bottles were used for each incubation temperature. Bottles were capped but not purged with nitrogen after the initial opening. PV were measured in triplicate, with each bottle sampled at each time point, following AOCS Official Method Cd 8-53 [16]. Samples stored at 4 °C were initially tested weekly, but then were tested monthly after 3 months of testing. Samples stored at 20 °C were tested weekly, while samples stored at 30 and 40 °C were tested every 3 days. Samples stored at 60 °C were analyzed daily. Different

sampling periods were necessary to capture the variation in PV with changing oxidation rates. After removing an aliquot for sampling, each bottle was recapped and returned to the test temperature. Testing was stopped when an average peroxide value of 5 mequiv/kg was reached, as this is the maximum accepted value for fish oil as recommended by the Global Organization for EPA and DHA [15].

Determination of Rate Constants and Shelf Life Prediction

Kinetic analysis of data was carried out using methods adapted from Labuza [17], Labuza and Bergquist [18], Spears et al. [19] and Tan et al. [20]. Pseudo-first order conditions were assumed with the oil substrate in excess so that

$$-\mathrm{d}[\mathrm{O}_2] = \mathrm{d}[C]/\mathrm{dt} = kC \quad (1)$$

where C is the concentration of oxidation products, in this case the PV, and k is the rate constant. Integration leads to the classic relationship in first order kinetics:

$$\ln C = \ln C_\mathrm{o} + kt \quad (2)$$

where C_o is the initial concentration of oxidation products (PV at initial times) and t is time in days. Plots of ln PV versus time were linear with slopes of k for most trials. Rate constants derived from linear plots were then fit to an Arrhenius model:

$$\ln k = \ln A - E_\mathrm{a}/RT \quad (3)$$

where A is the prefactor, R is the universal gas constant, T is the absolute temperature and E_a is the activation energy in J/mol.

Because the ultimate goal of this study was to investigate the validity of shelf life prediction by extrapolating rate constants from high temperature to low temperature studies, we therefore examined the exponential relationship between the time require to reach the upper limit of acceptability (t_rej) and temperature, according to

$$t_\mathrm{rej} = ae^{T} \quad (4)$$

where a is a constant and t_rej is the time required to reach PV = 5 mequiv/kg, as the upper limit of acceptability for fish oil oxidation. Integration of this relationship gives

$$\ln t_\mathrm{rej} = a + \ln T \quad (5)$$

suggesting that a plot of ln t_rej versus T should be linear.

Results and Discussion

Fatty Acid Analysis

The amounts of EPA and DHA present in both the 18:12 and concentrate oils (Table 1) differed, as expected from their label claims. The 18:12 oil had a label specification of 269 mg/g while the concentrate specified 430 mg/g. Upon testing, both samples exceeded label claims for EPA and DHA with values of 286 and 499 mg/g, respectively. We therefore considered these oils to have significantly different PUFA contents. Complying with label claims was also important to establish that these oils were typical of commercial products currently available; the purpose of this study was to monitor oxidation in commercial products with added antioxidants and flavors that contained FA at expected levels.

Table 1 EPA and DHA content (mean ± SD) of 18:12 oil and concentrate oil compared to the label claim

	18:12	Concentrate
Omega-3 claim (mg/g)*	269	430
Actual EPA content (mg/g)	151 ± 0.97	349 ± 1.23
Actual DHA content (mg/g)	135 ± 1.23	150 ± 0.42
Total EPA + DHA content (mg/g)	286 ± 1.56	499 ± 1.30

* Manufacturer guarantees only the total sum of EPA+DHA, not the individual fatty acid content

Stability Studies

In the experimental design, pseudo-first order kinetics was assumed. For the initial setup, each bottle contained approximately 180 ml of fish oil with approximately 20 ml of headspace. This corresponds to approximately 0.6 mol of FA and 2×10^{-4} mol of O_2, with FA present in excess of 3,500 times the amount of O_2. This ensures that O_2 is limiting, a necessary criteria of pseudo-first order reactions. Even in the samples that had the longest testing period (22 time points, with 5 ml of oil being used at each point), this situation was maintained with 70 m of oil, and 130 ml of air. This is equivalent to 0.23 mol of FA and 1.3×10^{-3} mol of O_2, ensuring that FA were still present in excess of 176 times the amount of O_2. Resulting plots of PV versus time were therefore expected to increase exponentially over time (Fig. 1a, b) with linear fits for the corresponding regressions of ln PV versus time (Table 2). It should be noted that kinetics are typically modeled by monitoring the breakdown of reactants, while this study monitors the formation of oxidation products. Oxidation products have been used by a number of research groups including Labuza and Bergquist [18], Mancebo Campos et al. [21], and Gomez-Alonso et al. [22] to successfully model oxidation kinetics.

Despite ensuring that pseudo-first order conditions were met, the reaction was obviously not first order for several of the sample-temperature combinations. For example, at 4 °C the 18:12 oil showed a clear lag in the onset of oxidation (Fig. 1a) that did not fit the expected model. In fact,

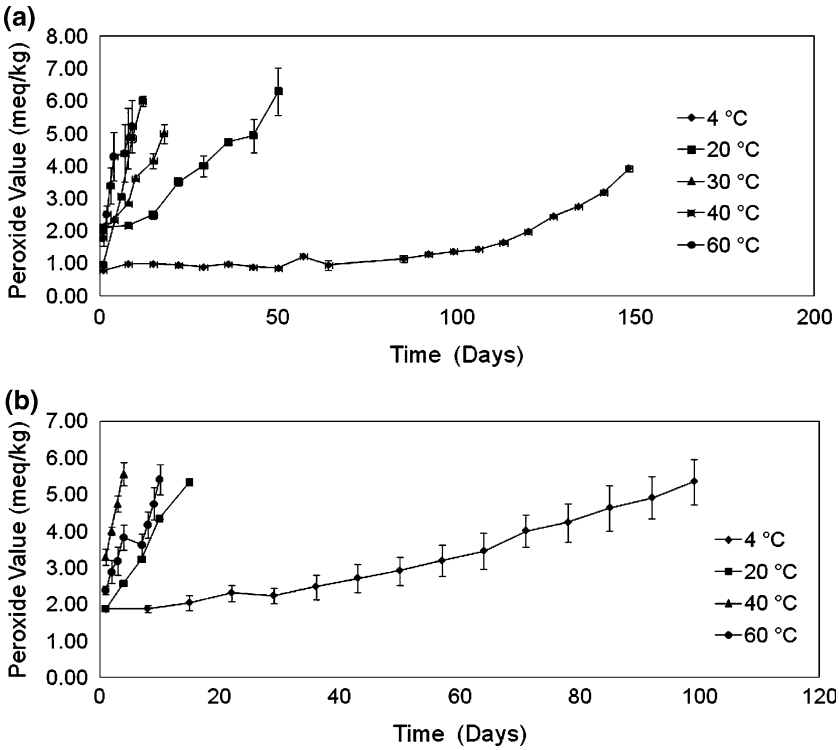

Fig. 1 Change in hydroperoxide value (mean ± SD, $n = 3$) at different temperatures over time. **a** 18:12 oil and **b** fish oil concentrate

Table 2 Testing temperatures, rate constants and coefficient of determinations for 18:12 oil and concentrate oil

Temperature (K)	18:12 oil		Concentrate oil	
	Rate constant (k days^{-1})	SD	Rate constant (k days^{-1})	SD
277	0.009	0.00	0.011	0.09
293	0.023	0.11	0.075	0.00
303	0.053	0.06	N/A	N/A
313	0.170	0.03	0.174	0.04
333	0.111	0.08	0.073	0.10
R^{2a}	0.822	–	0.524	–
R^{2b}	0.981	–	0.938	–

[a] Includes 60 °C data

[b] Excludes 4 and 60 °C data (18:12) or 60 °C data (concentrate)

modeling with zero and second order kinetics did not show any improvement at that temperature. Interestingly, the concentrate oil did follow a first order model quite well at 4 °C (Fig. 1b; Table 2), likely because of the absence of a prolonged lag phase. Both oils also deviated from the expected first-order model at 60 °C. This was less surprising as it is well accepted that the mechanisms for a complex chain reaction such as lipid oxidation may vary with increasing temperature [11]. For the purpose of this study, it was assumed that peroxide derivatives of fatty acids do not degrade; however, a large variety of secondary oxidation products are formed from these compounds as oxidation progresses. It may be that the increase in temperature increased the rate of both peroxide formation and breakdown; thus, the low rate constant derived at 60 °C for both oils suggests that peroxides are decomposing faster than they are being formed [9, 11]. Additionally, at elevated temperatures, lipid oxidation is more dependent on the concentration of oxygen. At high temperatures, the solubility of oxygen decreases, and becomes a limiting factor in lipid oxidation reactions as oxygen is rapidly consumed [11].

First-order kinetics were expected because of the experimental design, but all data was also evaluated for fit to a zero- and second-order model (Table 3). For a zero-order model, regression of PV versus time is linear, while for second-order models, one expects plots of 1/PV versus time to be linear. Coefficients of determination were simply used to assess fit (Table 3). In most cases it is quite obvious that a first-order model is as good as or better than other models (e.g., 18:12 oil at 20 and 30 °C). In other cases it is less obvious. For example, at both 40 and 60 °C for the 18:12 oil, a zero-order model has a slightly better fit to the data, while at 4 °C, the second order model has the best fit for the same oil. This is likely related to the high content of rapidly oxidizing PUFA that are present in fish oil.

Table 3 Coefficients of determination for 18:12 and concentrate fish oils when zero, first and second-order models were considered

Temperature (°C)	# of points	Zero-order	First-order	Second-order
18:12 Oil		r^2		
277	20	0.6993	0.8142	0.8648
293	8	0.9596	0.9429	0.9703
303	6	0.9752	0.9801	0.9572
313	4	0.9941	0.9539	0.8546
333	7	0.8777	0.8027	0.7052
Concentrate Oil		r^2		
277	15	0.9561	0.9876	0.9863
293	5	0.9429	0.9706	0.9105
313	4	0.9993	0.9969	0.9817
333	8	0.8812	0.8866	0.8603

All trials were stopped when the upper level for acceptability for fish oil, PV = 5 mequiv/kg, so that the duration of the experiment grew shorter as temperature increased. With daily sampling, this meant that fewer data points were acquired as temperature increased, making it difficult to fully capture the change in oil quality with time. The situation reached an extreme at 40 °C with both oils only requiring 4 days to exceed the upper limit of acceptability. Had sampling continued beyond this time point, the change in slope that is expected with first-order kinetics may have been captured. As plotted here, it is likely that only a small linear portion of a larger curve is being shown. Because we were only trying to model kinetics until the quality limit was reached and first-order kinetics fit well for 20 and 30 °C, it seemed appropriate to continue to model with first-order kinetics at the other temperatures. In addition, we were very reluctant to fit the data to a zero-order model in any situation. Zero-order kinetics dictates that reaction rate is independent of substrate concentration. Though both oils contain the same amount of fatty acid structures, the concentrate sample contained more PUFA, or substrate, that could be oxidized. Rates were obviously higher in the concentrate oil (Fig. 2; Table 2) so zero-order kinetics were ruled out immediately as an increase in PUFA increased the rate of peroxide formation. Finally, a first-order model was expected because others have found that oils containing antioxidants follow such models [17]. All this evidence pointed to the use of a first-order model when any ambiguity in model fit was encountered.

Arrhenius Behavior and Shelf Life Prediction

Rate constants for both oils were lower at 60 than at 40 °C; this result, combined with their poor fit to the first-order model, led to their exclusion from the Arrhenius plot. Similarly, because of the obvious lag time for onset of

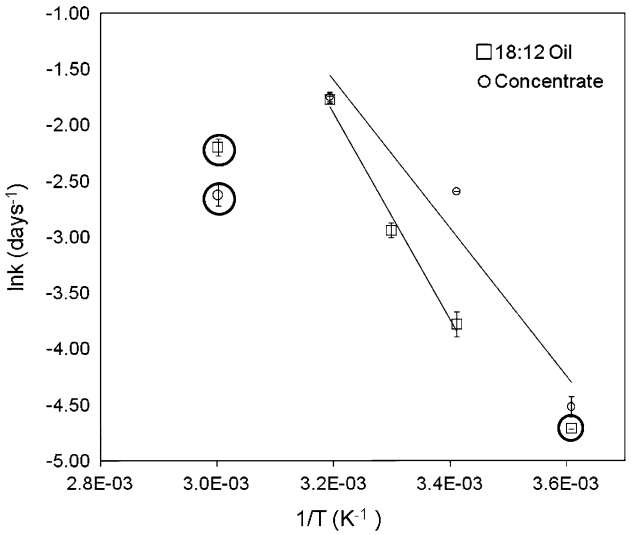

Fig. 2 Arrhenius plots for 18:12 oil (R^2 0.9871) and concentrate oil (R^2 0.9384). *Circled points* are not included in regression. Data are means ± SD

oxidation of 18:12 oil at 4 °C, the data collected at this temperature was also omitted from the plot for 18:12 oil, leaving only 3 data points for each oil. Despite the low sample numbers, we still see a good fit for both oils, with differing slopes. From the slopes, E_a of oxidation for the 18:12 and concentrate oils were calculated as 76 and 55 kJ/mol, respectively. The lower E_a for the concentrate oil was expected because less energy should be required to initiate oxidation due to the higher PUFA content. If the 4 °C data point is included in the 18:12 analysis (data not shown), the slopes are virtually identical, giving a very similar and highly unlikely E_a. This further points to the appropriateness of omitting the 4 °C data point in the 18:12 set. The E_a determined here are similar to those reported by Labuza [23] for lipid oxidation by free radical mechanisms (63–105 kJ\mol). With pure triglycerides (TAG), consisting of esterified DHA, Yoshii et al. [14] found similar E_a ranging from 77 to 97 kJ/mol, depending on the level of antioxidant added, and clearly showed that E_a increases with increased concentration of rosemary extract. With added antioxidants, both the fish oils examined here and those containing high levels of PUFA studied by Yoshii et al. [14], had E_a more similar to the stable vegetable oil from canola [24], pointing to the clear advantage of employing antioxidants to prevent oxidation.

The objective of this study was to determine the real time shelf life of these products by extrapolating from accelerated data. Data from experiments above 40 °C were therefore omitted from the shelf life plots (Fig. 3). This also agrees well with the recommendation by Frankel [11] that the temperature used for accelerated fish oil stability studies should not exceed 40 °C. This has obvious implications for fish oil stability studies that involve the use of

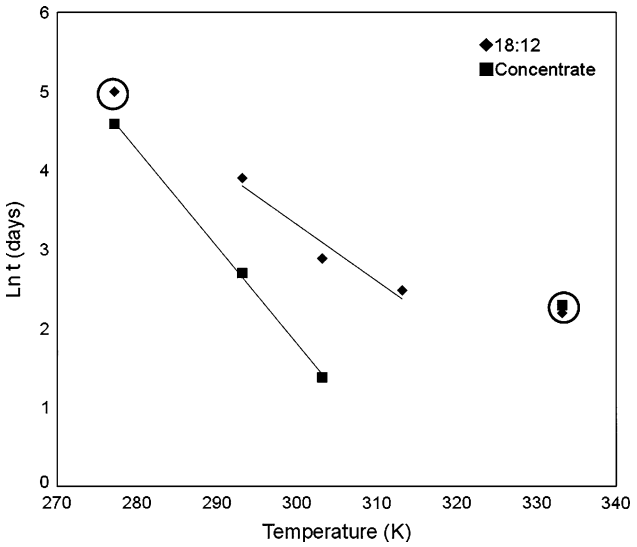

Fig. 3 Shelf life plots for 18:12 and concentrate fish oils. *Circled points* are not included in regression

oxygen absorption methods at elevated temperatures such as such as the Rancimat and Oxidative Stability Index (OSI) [25–27]. It is clear from the present study that PV of oils stored under Rancimat or OSI conditions will not be related to the PV of the same oils stored at temperatures <60 °C. Knowing that, the data for 4 °C in the 18:12 oil did not follow first order kinetics also led to its omission from the shelf life plot. Without that data, it is of course not possible to predict shelf life at temperatures <20 °C and >4 °C by interpolation. However, if the 4 °C data was included, the slope of the line would only change subtly so that the shelf life would be predicted at 143 days rather than the measured 148 days. This represents an error <4% and when considering data between 4 and 20 °C, the impact would be proportionally and absolutely less. Thus, one may cautiously extrapolate beyond the linear portion of the curve for 18:12 oil, knowing that the predicted shelf life would be under-estimated by no more than 4%. It is important to note that these equations only hold true for these specific products. Oils that have different fatty acid or lipid class profiles or use different antioxidants will likely have different rates of oxidation.

This study was designed to mimic the oxidation that might take place after a consumer has purchased a bottle of fish oil and has begun consuming it. The shelf lives measured here for storage at 4 °C for both oils (148 and 99 days for 18:12 and concentrate, respectively) agrees well with typical manufacturers' recommendations of 90 days in refrigeration. An obvious contrast is with freshly bottled fish oils, purged with inert gas, usually nitrogen. Exclusion of air in such products promotes much longer-term oxidative stability and we would not expect the kinetics of oxidation to be similar to those reported here. Studies to monitor such products would be logistically difficult to organize simply because sealed containers of oil could only be sampled once; after opening, the sample would be in contact with air and, even if again purged with nitrogen, rates of oxidation would be expected to vary. Thus, a very large amount of individually bottled oil would be required.

The lack of kinetic data between 4 and 20 °C is the largest flaw in this study. Had we included at least one data point in this range, we would have been much better able to characterize both the Arrhenius behavior and shelf life prediction. This is critical because it would have set a lower limit on temperatures to which we could interpolate without introducing a known minimum error. It would also have been useful to examine other measures of oxidation. Frankel [28] used volatile oxidation products to examine the kinetics of fish oil oxidation. Anisidine values are also recommended in the GOED Voluntary Monograph [15] as a quality measure of fish oil. These tests could allow us to investigate the relationship between primary and secondary oxidation and could help to determine if hydroperoxides are in fact breaking down at 60 °C. A substantial increase in either anisidines or volatile oxidation products would support our hypothesis of peroxide breakdown. Additionally, monitoring secondary oxidation would allow for the creation of shelf life plots that could potentially correlate with sensory characteristics of the oils and give a better indication of how consumers will perceive the oils. However, both parameters are difficult to accurately measure in commercial oils that have added flavors. Our experience has shown that flavor compounds co-elute with oxidation products in gas chromatographic analysis of volatiles, especially when headspace analysis techniques are utilized. While selective ion monitoring could potentially be used to monitor oxidation in co-eluting peaks, these techniques are beyond the scope of this paper. Flavor compounds also interfere with the *p*-anisidine test, causing drastic overestimation of the measure, sometimes outside the range of measurement. Thus, monitoring change in secondary kinetics with *p*-anisidine test would only be feasible in unflavored oils, which would not necessarily be relevant for shelf life studies of commercial dietary supplement.

Fish oil is a popular dietary supplement taken by many people for its health benefits. Because of the high PUFA content, the oil oxidizes rapidly. At temperatures ≥20 °C and ≤40 °C, 18:12 fish oil appears to follow first-order kinetics. Fish oil concentrate demonstrates first-order kinetics at temperatures ≥4 °C and ≤40 °C. At 60 °C both oils oxidized more rapidly, likely because of hydroperoxides breaking down faster than they could form. This confirms that accelerated stability studies using fish oil should be conducted at temperatures no higher than 40 °C. Accelerated temperature data can then be used to predict

shelf-life at lower temperatures; however, extrapolation of data should be done with caution as the rate of reaction may not hold true at low temperatures. This was the case for 18:12 oil as clearly demonstrated in this study.

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