# Hexanal Formation via Lipid Oxidation as a Function of Oxygen Concentration: Measurement and Kinetics

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## ABSTRACT

A system was developed to continuously quantify hexanal produced via lipid oxidation of oils at constant oxygen concentrations. Two kinetic models were derived from molecular mechanisms of oxidation to describe the initial (a cubic model) and accelerated (an extended model) stages of oxidation. The kinetic models illustrated the mechanistic influence of oxygen on rate constants and fit the data as well as simplistic curve fitting models. The monomolecular reaction phase showed the expected hyperbolic fit of inverse rate vs reciprocal oxygen concentration. The break point between initial and accelerated stages as function of oxygen concentration was represented by a logarithmic function.

## INTRODUCTION

LIPID OXIDATION is one of the main deteriorative reactions in microbiologically stable dry and semi-moist foods (Lingnert and Eriksson, 1980). The kinetics of lipid oxidation through a free radical mechanism have been described in detail (Dugan, 1976, Frankel et al., 1981; Karel, 1986; Labuza, 1971; Nawar, 1985; Paquette et al., 1985a, b). The classical autoxidation scheme is commonly employed to illustrate the molecular mechanisms in which lipid oxidation is divided into initiation, propagation and termination steps. Kinetics of lipid oxidation through a free radical mechanism in the initiation and propagation stages have been described using both mechanistic equations and statistically based zero order and exponential curve fitting equations respectively (Labuza, 1971; Hall et al., 1985). The time at which the initial stage of monomolecular hydroperoxide decomposition catalyzed oxidation ends and the more rapid bimolecular catalyzed phase begins is defined as the break point ($T_b$). $T_b$ is generally near the threshold point of a sensorially unacceptable product (Labuza, 1971). The threshold point occurs when the peroxide volatile breakdown products reach a high enough level in the headspace to cause an off odor (Nawar, 1985). This usually occurs prior to the maximum peroxide value (Labuza, 1971).

Linoleic acid, a predominant unsaturated fatty acid in many food products, can be oxidized to hexanal, octanal, and 2,4 decadienal which further decomposes into hexanal. These headspace volatiles and especially hexanal have been commonly used to gauge the extent of lipid oxidation. The odor threshold value of hexanal in cereals is approximately 0.15 ppm (Fritsch and Gale, 1976).

Numerous solutions to reduce lipid oxidation include adjusting the water activity of dry foods close to the monolayer, adding antioxidants, reducing the amount of unsaturated fat added, degassing to remove residual oxygen and gas flushing with nitrogen or vacuum packaging. A good barrier to both oxygen and water vapor is then required to maintain desirable conditions. To further minimize the reaction, exposure to high temperature and light during distribution must be reduced (Quast and Karel, 1972).

Maintaining low oxygen levels within a package is a viable approach to retard lipid oxidation (Deobald and McLemore, 1964). However, the presence of minimal (in some cases as low as 1%) oxygen in the package headspace can lead to product quality losses since the amount of oxidized fat which will produce off-odor is generally assumed to be very small yet little data exist (Tamsma et al., 1964; Labuza, 1971). Thus, to accurately assess the stability of a food product to lipid oxidation, strict control of oxygen concentration under test conditions is required to determine what level of oxygen could be tolerated, within economic limits, to give the desired shelf life.

Unbreit et al. (1964) described a closed system to quantify the rate of oxygen consumption using a Warburg apparatus. In the Warburg system, the level of oxygen decreases as it is consumed by the substrate and thus the reaction rate becomes dependent upon the new oxygen level, the achieved peroxide level and amount of remaining oxidizable substrate, (especially below 5% oxygen, Frankel et al., 1981; Karel, 1986). Quast and Karel (1972) somewhat alleviated the problem of changing oxygen concentrations by periodically injecting air or the desired oxygen level at selected time intervals into the Warburg flasks. However, the oxygen concentration still fluctuated within the test cell due to time intervals between oxygen replacements. Hall et al. (1985) developed another system to allow for a high and constant oxygen concentration flow through the test cell. They did not study low oxygen levels. Amount of headspace volatiles produced from samples within the test cells was used as an index of lipid oxidation in both systems.

The purpose of our study was to develop a continuous system to quantify lipid oxidation at constant oxygen concentrations by continuously monitoring the rate of hexanal formation as an index of lipid oxidation. Data were then analyzed based on both curve fitting equations and kinetic models developed for the molecular mechanism of hexanal formation as a function of oxygen concentration in the headspace.

## Materials & Methods

### Model system

A freeze-dried model system was composed of soybean oil as oxidizable substrate (8.38 g soy oil, Hain Pure Food Company, Los Angeles, CA), distilled and deionized water (59.06 mL), Tween 20 (0.01g), and microcrystalline cellulose (32.45 g, CMC PH 101 Food Manufacturing Corp., Philadelphia, PA.). Ingredients were mixed sequentially at high speed in a domestic blender. Initial moisture content (dry basis) was determined gravimetrically using a modification of the AOAC procedure (AOAC, 1985; Koelsch, 1989). Moisture sorption isotherm data for triplicate samples were measured gravimetrically by measuring product weight change at seven relative humidities created by salt solutions (Rockland and Nishi, 1980). Equilibrium was reached when weight change (on a dry basis) did not exceed 0.1% (Labuza, 1984). Moisture content was 2g $H_2O$/100g solids. This is below the calculated BET monolayer value of 3.05g $H_2O$/100 g solids and in a range which would increase lipid oxidation rates (Labuza, 1971).

### Constant oxygen concentration apparatus:

The apparatus shown in Fig. 1 was developed to regulate oxygen, relative humidity, temperature, and light exposure and to continuously

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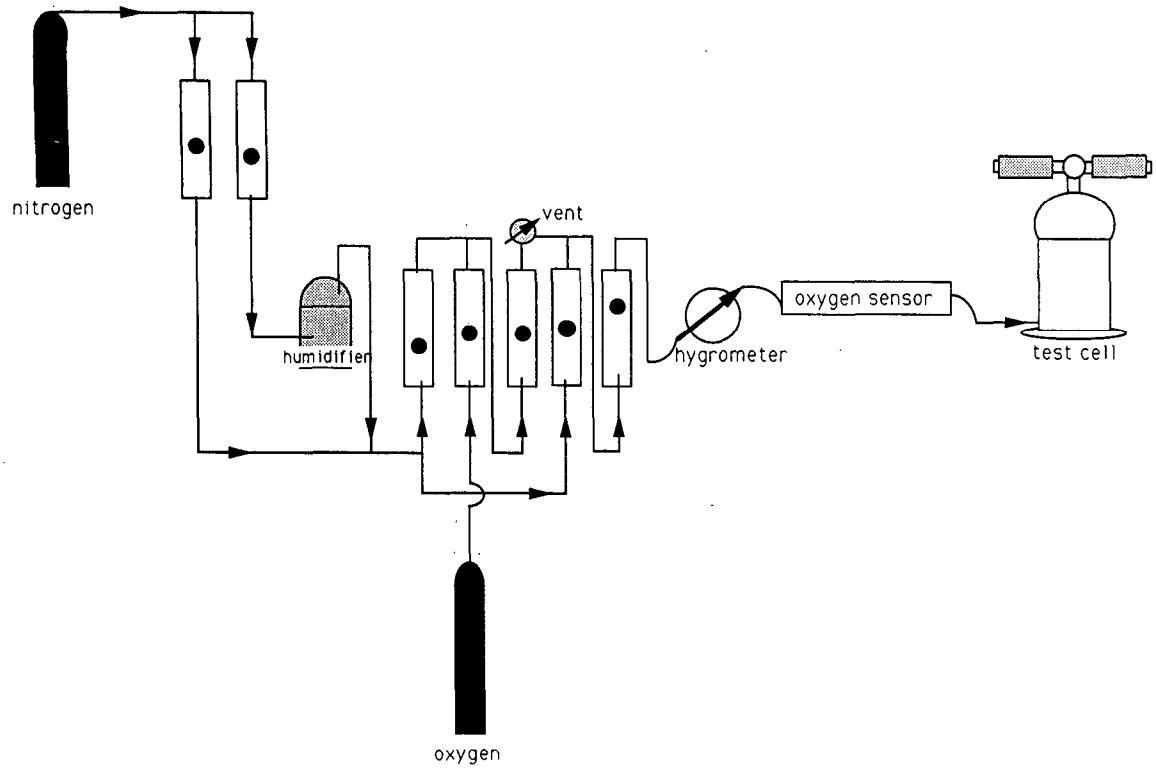


*Fig. 1—Schematic of apparatus for maintaining constant oxygen concentration with Tenax traps to continuously measure hexanal formation.*

quantify headspace hexanal produced from lipid oxidation. All experiments conducted at various oxygen concentrations were done at 23 ± 1% relative humidity, 23 ± 2°C in the absence of light. Swagelok fittings (Crawford Fitting Co., Solon, OH) were used to connect the copper tubing, rotameters (Cole Palmer, Chicago, IL) and glass test cells (modified 40/50 gas washing bottle, Ace Glass Inc., Vineland, NJ.).

In the apparatus, nitrogen gas was humidified to a controlled relative humidity and pure oxygen was diluted and mixed with it. An exhaust valve continuously released a controlled amount of oxygen/nitrogen mixture which allowed for sufficient volume in the gas stream for a second dilution with humidified nitrogen gas. The two dilutions provided the necessary accuracy and precision to maintain low and constant oxygen concentrations. Relative humidity (Hygrodynamics, Silver Springs, MD.) and oxygen concentration sensors (Servomix, London, England) measured the gas mixtures prior to oxygen/nitrogen flow into the oxidation test cell. Two test cells were used for continuous headspace sampling to ensure the amount of oxidizable substrate was the limiting factor at all oxygen concentrations. Prior to testing the system at each oxygen concentration, the gas flow was channeled through an equilibration cell. The oxygen concentration was considered stable if it did not fluctuate more than 1% and relative humidity 0.1 % over 2 hr. Once stabilized, the product was placed in the test cell and a gas flow of 48 mL/min was channeled through this cell. Gas flow out of the cell was filtered through a Tenax trap (0.4g of 80/100 mesh Tenax, Ohio Valley Specialty Chemical)). At predetermined time intervals, flow from the cell was switched to an alternate Tenax trap and the sample Tenax tube removed for analysis. To extract hexanal from the Tenax trap, 1.5–2.0 mL of HPLC grade 2-methylbutane (Aldrich Chemical Co., Milwaukee, WI.) was dripped through the filled capillary tube and collected by centrifuging at 750 rpm (International Equipment Co., Boston, MA.). The extractant was concentrated under nitrogen to a 0.5 mL. Recovery studies in triplicate showed a 74 ± 4% recovery of hexanal which was used as a correction factor.

A 5890 Hewlett Packard gas chromatograph equipped with dual flame ionization detectors (F.I.D.) and a Hewlett Packard 3392A integrator was used to quantify hexanal from 1 mL aliquots of sample in a cooled 5.0 mL syringe (Hamilton Co., Reno, NV.). The column was bonded Carbowax 20M (Supelco Inc., Bellefont, PA). Gas chromatograph conditions were initial temp 40°C for 10 min and 2°C/min increase until reaching 120°C, injection port 200°C and detector 250°C. Helium flow was 31 to 33 mL/min. A calibration factor ($C_f$) of hexanal was determined by use of an external standard.

### Derivation of kinetic models

Mathematical models based on the molecular mechanisms of oxidation for production of hexanal, were derived for both initial monomolecular hydroperoxide decomposition period and the more rapid bimolecular stage of oxidation. In general, the rate at which the oxygen reacts with unsaturated lipid, as a function of oxygen pressure is:

$$\frac{\partial O_2}{\partial t} = \frac{[R_i]^{1/2}[RH][O_2]}{k_\alpha[RH]+k_\beta[O_2]} \quad (1)$$

where $[O_2]$ is the oxygen concentration, [RH] the substrate concentration, $k_\alpha$ and $k_\beta$ are constants, $R_i$ is the rate of initiation and is equal to $k_{mono}$ [ROOH] for the initial monomolecular stage of peroxide [ROOH], decomposition. As each oxygen molecular reacts in the propagation steps, one peroxide molecule, [ROOH], forms, thus:

$$\frac{\partial[\mathrm{ROOH}]}{\partial t} = \frac{\partial[O_2]}{\partial t} = \frac{[R_i]^{1/2}[RH][O_2]}{k_\alpha[RH]+k_\beta[O_2]} \quad (2)$$

As shown by Labuza (1971) at high levels of oxygen in the headspace, $k_\alpha$ [RH] << $k_\beta[O_2]$ and thus the rate is independent of oxygen concentration so that:

$$\frac{\partial[ROOH]}{\partial t} = k_p[ROOH]^{1/2} \quad (3)$$

where $k_p$ is the overall rate constant for the monomolecular period. This takes into account all the rate constant terms and should be independent of oxygen level in this upper range. At low levels of the extent of oxidation, i.e. when the substrate concentration does not change significantly, rate of formation of peroxides as a function of time is thus found by integration of Eq. (3) to give (Maloney, 1966; Labuza, 1971):

$$[\mathrm{ROOH}]^{1/2} = \frac{k_p}{2} t = k_m t \quad (4)$$

In this case $k_m$ is now the rate constant in units of (concentration)$^{1/2}$

unit time which is from the slope of a plot of square root of peroxide value vs time.

The formation of breakdown products of peroxides such as hexanal from a mechanistic standpoint is monomolecular and thus the rate of hexanal production is directly proportional to the peroxide level, [ROOH]:

$$\frac{\partial[H]}{\partial t} = k_h\,[ROOH] \tag{5}$$

where [H] is the hexanal concentration (ppm) at time t and $k_h$ is the rate constant for hexanal formation in reciprocal time units. This assumes that the disappearance of hexanal, for example by the Maillard reaction, is much slower than its formation rate during lipid oxidation. By substituting Eq. (4) into Eq. (5), and combining the rate constants for peroxide ($k_m$) and hexanal ($k_h$) formation rates into an overall rate constant ($k_1$) and integrating, the hexanal concentration can be expressed as a cubic model:

$$[H] = [H_o] + \left(\frac{k_1}{3}\right) t^3 \tag{6}$$

where $H_o$ is the initial hexanal concentration and $k_1/3$ is the combined rate constant in units of concentration/(time)$^3$ where $k_1 = k_h k_{m2}$. Thus a plot of the cube root of hexanal concentration (minus the initial value $H_o$) vs time should give a straight line with slope the cube root of $k_1/3$.

In the bimolecular oxidation phase, when peroxides begin to degrade faster than produced, the rate of formation of hydroperoxides can be described as (Labuza, 1971):

$$[ROOH] = \frac{[RH_o]}{(1+e^{-k_2 t})} \tag{7}$$

where $RH_o$ is the initial lipid concentration in moles/liter and $k_2$ is the bimolecular hydroperoxide decomposition rate constant in reciprocal time units (Labuza, 1971). This results from a plot of the natural log of the peroxide concentration vs. time.

Again assuming the rate of hexanal formation is proportional to the peroxide concentration by Eq. (5) and substituting Eq. (7) in Eq. (5), the rate of hexanal formation is:

$$\frac{\partial\,[H]}{\partial_t} = \frac{k_h\,[RH_o)]}{(1+\,e^{-k_2 t})} \tag{8}$$

Integration of this equation results in the equation to describe the extent of hexanal formation as a function of time in the latter stages after the hexanal reaches the break concentration [$H_t$], then:

$$[H] = [H_t] + k_h\,[RH_o]\left(t + \frac{\ln(1+e^{-k_2 t})}{k_2}\right) \tag{9}$$

As seen by the nature of this equation there is no simple form for plotting a function of hexanal vs time as for the monomolecular stage, thus some type of nonlinear regression solution must be used to obtain the values of $k_h$ and $k_2$.

In all derivations above we assumed the oxygen concentration was not limiting and remained constant. Very little data are available for the point at which the oxygen concentration limitation becomes important in Eq. (1) but it is known that it is a function of water content, temperature and nature of the surface the lipid is on (Marcuse and Frederiksson, 1968; Labuza, 1971). For example Simon et al. (1971) found it to be about 10% oxygen for freeze dried salmon.

By simplifying and rearranging Eq. (1), which is the form of a parabola of the rate of peroxide formation (or oxidation) vs oxygen concentration, we can show that the equation takes the form of a straight line if the reciprocal of the rate is plotted vs the reciprocal of the oxygen concentration. This would hold up to the concentration of oxygen which just becomes non-limiting as was found by Simon et al. (1971) and derived by Labuza (1971). The equation is:

$$\frac{1}{\partial[ROOH]\,/\,\partial_t} = \frac{1}{k_a\,[ROOH]^{1/2}}\left[1 + \frac{k_b}{[O_2]}\right] \tag{10}$$

The values of $k_a$ and $k_b$ are from the fit of the parabola and take into account all combined rate constants and the substrate concentration. If the oxygen concentration is maintained constant, as in our study, then for the initial stages of peroxide formation and hexanal formation when the substrate concentration changes little the following form of the equation is found:

$$\frac{\partial\,[ROOH]}{\partial_t} = \frac{k_a\,[ROOH]^{1/2}\,[O_2]}{[O_2] + k_b} = k_p\,[ROOH]^{1/2} \tag{11}$$

Note to obtain Eq. (11), in Eq. (1), the right hand side is divided at the top and bottom by $k_b$ and the change in [RH] is assumed small. Thus for constant oxygen pressure, the monomolecular region rate constant, $k_p$, now becomes a function of the oxygen pressure, where:

$$k_p = \frac{k_a\,[O_2]}{[O_2] + k_b} \tag{12}$$

and, as with the reaction rate, rearranging gives:

$$\frac{1}{k_p} = \frac{1}{k_a} + \frac{1}{k_b\,[O_2]} \tag{13a}$$

Thus from Eq. (6) for hexanal production as a function of the time, the overall rate constant for hexanal formation in the monomolecular initial oxidation phase, $k_1$, should also be proportional to the oxygen level by this same relationship. This can be derived as follows, substituting in Eq. (13a), the various transformations of the rate constants previously derived:

$$\frac{2\sqrt{k_h}}{\sqrt{k_1}} = \frac{1}{k_a} + \frac{1}{k_b\,[O_2]} \tag{13b}$$

Thus a plot of reciprocal of the square root of the rate constant $k_1$ for hexanal formation from Eq. (6) vs reciprocal of the oxygen concentration, if oxygen concentration is kept constant, should be a straight line. This assumes that $k_h$ is independent of oxygen concentration.

A similar derivation can be made for the advanced bimolecular decomposition stage of oxidation based on Eq. (7) and (10) where:

$$\frac{\partial[ROOH]}{\partial_t} = \frac{[ROOH]\,[O_2]}{k_a + k_b\,[O_2]} \tag{14}$$

Again, assuming constant oxygen is maintained during the experiment, then:

$$\ln\left(\frac{[ROOH]}{[RH_o] - [ROOH]}\right) = \frac{[O_2]}{k_a + k_b\,[O_2]}\,t \tag{15}$$

or

$$[ROOH] = \frac{[RH_o]}{1 - e^{-\frac{[O_2]}{k_a + k_b\,[O_2]}\,t}} \tag{16}$$

Thus, based on Eq. (5), the concentration of hexanal as a function of time and oxygen level will be:

$$[H] = \frac{k_h\,[RH_o]}{1 - e^{-\frac{[O_2]}{k_a + k_b\,[O_2]}\,t}} \tag{17}$$

where

$$k_2 = \frac{[O_2]}{k_a + k_b\,[O_2]} \tag{18}$$

Based on this, at advanced stages of oxidation, $k_h$ as before should be oxygen independent and $k_2$ should follow the form of Eq. (18) since $k_2$ is hyperbolically related to the oxygen level and a plot of the reciprocals should give a straight line. No data exists to determine if the function no longer holds at the same oxygen level as for the monomolecular period.

As simple alternatives to these molecular mechanisms models, Hall et al. (1985) used a zero order model for the initial stage (19) and an exponential model (20) for the accelerated stage in the form:

$$[H] = [H_o] + k_z\,t \tag{19}$$

$$[H] = [H_o]\,e^{k_e t} \tag{20}$$

where $k_z$ and $k_e$ were statistically fitted rate constants. Neither of these models or rate constants showed any theoretical relationship to oxygen level.

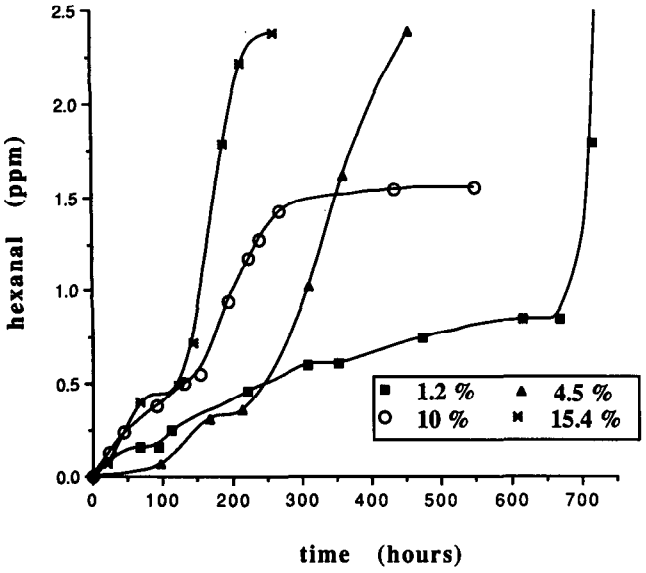


*Fig. 2—Hexanal formation as function of time for oxidation of soybean oil at 23°C and four levels of constant oxygen concentration.*

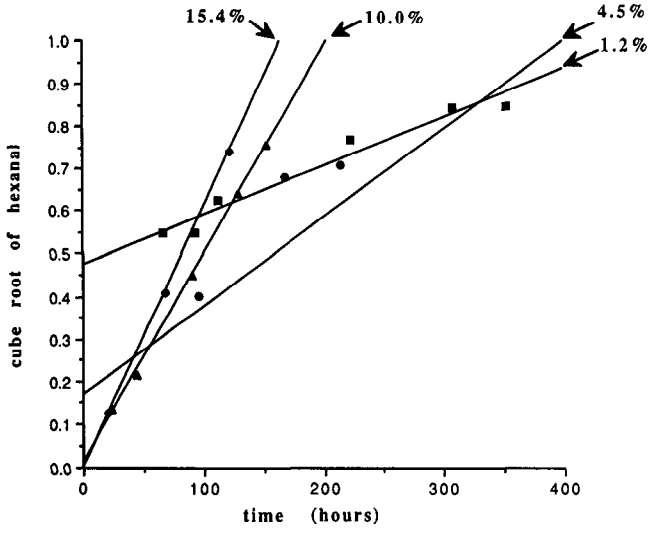


*Fig. 3—Cube root of hexanal formed vs time (Eq. 6) for initial stage of monomolecular hydroperoxide decomposition during oxidation of soybean oil at 23°C for different oxygen concentrations. Statistical fit results given in Table 1.*

Data from our study were analyzed using both the statistical zero under (19) and exponential Eq. (20) and the derived kinetic models (6 and 9). Kinetic models were evaluated with either a linear regression as for the monomolecular breakdown phase or by a Newton-Gauss non-linear regression program from the HP Statistical Library (Hewlett Packard Model 9816).

## RESULTS

THE CONSTANT oxygen concentration apparatus performed as designed to maintain low oxygen concentration at constant relative humidity, light, and temperature conditions for continuously quantifying hexanal formation. The concentration of hexanal (ppm, w/w) in soybean oil as a function of time for 1.2, 4.5, 10.0 and 15.4 % oxygen is presented in Fig. 2. Figure 3 and 4 show representative plots for equations (5) and (9) based on kinetic models for monomolecular and bimolecular hydroperoxide decomposition regions at the four constant oxygen levels tested. The constants calculated for each of the

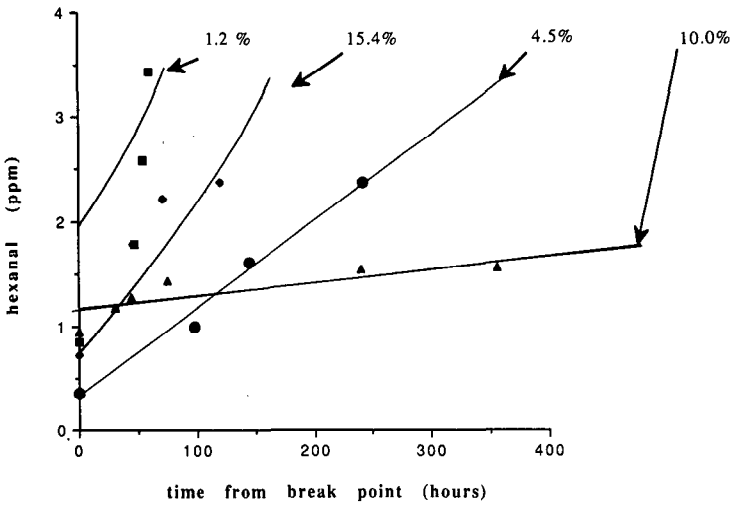


*Fig. 4—Hexanal concentration vs normalized time ($T-T_b$) for rapid bimolecular hydroperoxide decomposition period during oxidation of soybean oil at 23°C for different oxygen concentrations. Solid lines represent fit of data to Eq. (9) based on the mechanism. Statistical fit results given in Table 2.*

*Table 1—Rate constants for hexanal formation during monomolecular stage of lipid oxidation*

| | Cubic kinetic model (Eq. 6) | | | Zero order (Eq. 19) | | |
|---|---|---|---|---|---|---|
| | $(k_1/3 \times 10^3)^{1/3}$ ppm/hr$^3$ | SE* | | $k_z \times 10^3$ ppm/hr | SE* | |
| $\%O_2$ | 95% confidence limits | | $r^2$ | 95% confidence limits | | $r^2$ |
| 1.2 | 0.77 ± 0.27 | 0.058 | 0.89 | 1.33 ± 0.30 | 0.063 | 0.95 |
| 4.5 | 2.68 ± 11.13 | 0.074 | 0.90 | 2.53 ± 0.82 | 0.059 | 0.93 |
| 10.0 | 2.26 ± 0.09 | 0.032 | 0.95 | 3.20 ± 0.53 | 0.019 | 0.99 |
| 15.4 | 3.76 ± 22.30 | 0.126 | 0.82 | 4.15 ± 19.4 | 0.110 | 0.88 |

* Standard error

*Table 2—Rate constants for hexanal formation during accelerated stage of lipid oxidation*

| | Kinetic model (Eq. 9) | | | Exponential (Eq. 20) | | |
|---|---|---|---|---|---|---|
| | $k_h \times 10^3$ hr$^{-1}$ | $k_2 \times 10^3$ hr$^{-1}$ | | $k_e$ $10^3$ hr$^{-1}$ | SE* | |
| $\%O_2$ | 95% confidence limits | | SE* | 95% confidence limits | | $r^2$ |
| 1.2 | 12.11 ± 3.95 | 45.01 ± 9.05 | 0.660 | 7.69 ± 3.90 | 0.242 | 0.80 |
| 4.5 | 24.23 ± 25.01 | 9.41 ± 1.22 | 0.130 | 4.25 ± 4.24 | 0.172 | 0.90 |
| 10.0 | 1.37 ± 0.07 | 2.30 ± 0.09 | 0.154 | 12.14 ± 11.78 | 0.224 | 0.81 |
| 15.4 | 10.80 ± 0.87 | 17.77 ± 0.67 | 0.411 | 9.90 ± 14.90 | 0.300 | 0.80 |

* Standard error

statistical and kinetic expressions are presented in Tables 1 and 2 for the initial and accelerated phases respectively.

As shown in Table 1, the more kinetically appropriate cubic model and zero order models provided statistically comparable fits. The $r^2$ values ranged from 0.82 to 0.95 and 0.88 to 0.99 for the cubic and zero order models respectively. The standard error was of the same order of magnitude for both models. The cubic model of eq. (6) represents a mechanistic basis by which oxidation can be followed and predicted through the monomolecular oxidation phase, and as seen, is operable over the whole oxygen concentration range studied. Although a simple statistical model may fit better (higher $r^2$), from a kinetics standpoint is better to use a mechanistic model, since the components of that model have some theoretical basis and can be tested under different conditions such as for oxygen concentration dependence, as we have done, or temperature dependence based on the Arrhenius relationship.

The reciprocal of the rate constant for hexanal production ($k_1$) from the derived kinetic model for the initial monomolecular stage of oxidation is plotted against the reciprocal of oxygen concentration in Fig. 5 as a demonstration of Eq. (13b). As seen, the function fits over the whole oxygen concentration

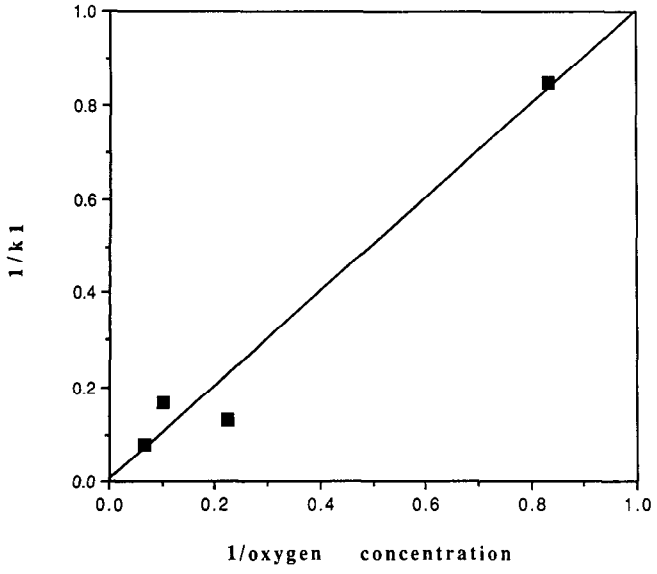


*Fig. 5—Hyperbolic plot of inverse of overall rate constant, $k_1$, for formation of hexanal during monomolecular initial oxidation stage vs inverse oxygen concentration showing fit of Eq. (13b) and dependence of rate constant on oxygen concentration.*

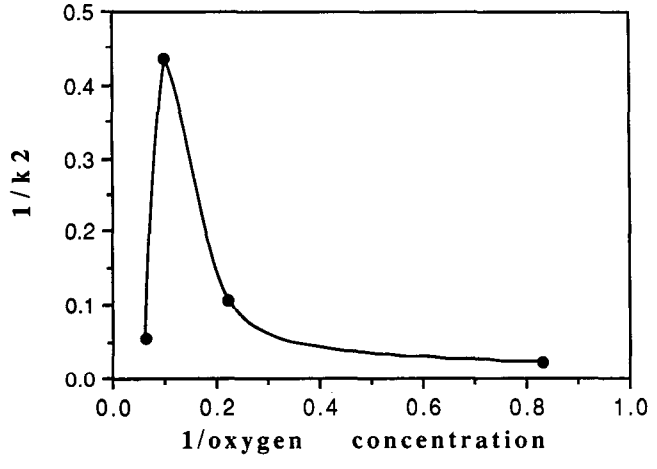


*Fig. 6—Hyperbolic plot of inverse of overall rate constant, $k_2$, for formation of hexanal during rapid bimolecular stage of oxidation vs inverse oxygen concentration showing lack of fit of Eq. (18) which theoretically should give a straight line.*

range with $r^2$ 0.96, showing oxygen dependence of the rate constant. One could derive the individual constants from this data but since only four oxygen values were used, their statistical significance would not be high. As seen there does not seem to be an upper critical oxygen level where the oxygen dependence disappeared. If this were so, the line would become asymptotic. Of course this is for soybean oil, and the relationship will differ for other foods.

Table 2 shows results for the accelerated stage of oxidation. Neither the kinetically based model or exponential equation provided a good fit for the data. The large confidence intervals associated with both the kinetic and exponential constants suggested need for more data. Theoretically $k_h$ should be independent of oxygen level but at 10% oxygen, the value was lower than the other oxygen levels. Again with only four test levels of oxygen, and with the lower number of points available in the rapid oxidation period, the differences of the values of $k_h$ may not be significant. An additional reason for this difference could be that the rate constants cannot be determined separately by the non-liner regression technique, so any error

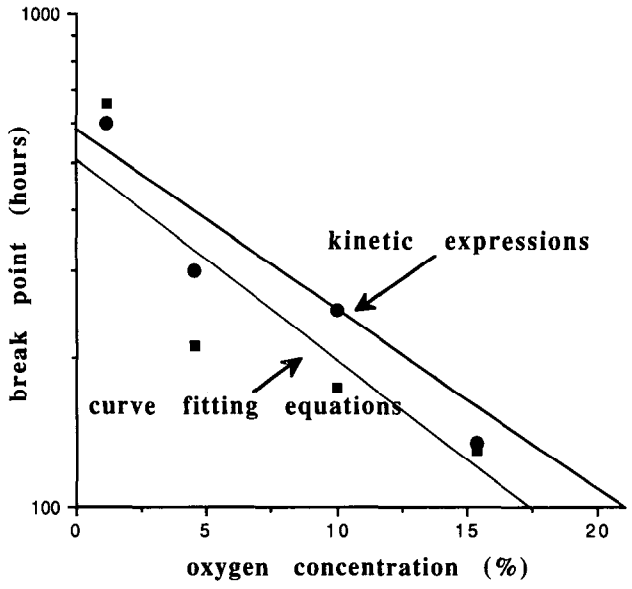


*Fig. 7—Breakpoint time between slow and rapid oxidation stages vs. oxygen concentration derived from mechanistic kinetic models and the statistical curve fitting models.*

in estimation of $k_2$ the oxygen dependent term would impact on the value of $k_h$.

Figure 6 shows the reciprocal of $k_2$ plotted versus the reciprocal of the oxygen concentration. The results did not fit the expected straight line for the hyperbolic function of Eq. (18). Above some critical level of oxygen, $1/k_2$ should be constant unless there was no critical level, otherwise it should increase, as was seen for the oxygen dependent constant in the monomolecular period. In this case between 10% and 1% there was an inverse function, exactly opposite that which the equation predicted, i.e. $k_2$ decreased as oxygen concentration increased. Reasons for lack of expected fit could be that breakdown of peroxides, into secondary products like hexanal as well as further reactions of hexanal and peroxides became significant. Since $k_h$ was not constant, there was a suggestion that this had occurred. In addition, as noted above, the lower number of data points at any oxygen level meant that the non-linear fitting routine may converge on a set of numbers that fits the line, as does the non-mechanistic exponential equation, however those sets of numbers (the rate constants) have no physical meaning. Published reports in food science kinetics have many examples of such improper fits (Stamp, 1990). More data in the 1 to 10% oxygen range is needed.

The breakpoint between the two stages of oxidation was found by setting the equations for each stage equal to each other and solving for break time. Again if the above equations are followed, the level of hexanal at the breakpoint, should be independent of oxygen level. An empirical logarithmic relation as shown in Fig. 7 was found with break point hexanal level increasing as oxygen level decreased. The break point determined from the kinetic models more closely fit the logarithmic plot, $r^2$ 0.93, than the curve fitting equations with $r^2 = 0.76$. Thus the kinetic models were more appropriate to predict break points at any oxygen concentration between 1.2 and 15.4%. Since the break point should be close to the end of shelf life of a food, this would be useful as a prediction model for any other oxygen level. These results also indicated that oxidation is very complex, and to predict stability of foods more data at many oxygen levels will be needed.

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