

Prediction of Decoloration in Paprika Oleoresins. Application to Studies of Stability in Thermodynamically Compensated Systems

M. Jarén-Galán, A. Pérez-Gálvez, and M. I. Mínguez-Mosquera*

Departamento de Biotecnología de Alimentos, Instituto De La Grasa (CSIC),
Avenida Padre García Tejero 4, Sevilla 41012, Spain

In six paprika oleoresins, the kinetic parameters for the decoloration reaction at three temperatures have been established. The thermodynamic study shows that the decoloration reaction in each oleoresin has its own activation entropy (ΔS) and activation enthalpy (ΔH). The six reactions studied show a constant ratio between ΔH and ΔS , which means that each reaction is an isokinetic form of only one reaction affected by thermodynamic compensation. Instead of one equation per oleoresin to predict pigment concentration as a mathematical function of time and temperature, one unique equation can be obtained in which ΔH is a function of ΔS . The validity of this equation has been tested by comparing the actual concentration remaining during a heat treatment and the calculated one. More than 90% of the calculated concentrations are within the range of variability of the actual mean. Due to the reduction in the number of variables in thermodynamic compensated systems, a general procedure to calculate the activation entropy in isokinetic reactions is proposed.

Keywords: *Compensated kinetic; carotenoids; oleoresin; degradation; decoloration*

INTRODUCTION

Stability, in all its aspects, is one of the objectives sought by the technological treatment of foodstuffs. The aim is to conserve the original qualities against deterioration in the product, or at least to know when properties are being lost and to what extent. For parameters affecting health, a limit can be established beyond which consumption is not safe. However, deterioration in other attributes can affect product quality very directly without affecting its aptness for consumption. Such is the case of foodstuffs that gradually, depending on environmental conditions, lose their aroma, color, or flavor. Additives and spices are especially prone to this.

Paprika oleoresin is a solution of carotenoid pigments in the oil of the fruit (Attuquayefio and Buckle, 1987; Cortijo et al., 1982). The chromatic properties, nonpolar character, and high concentration of the pigments make the oleoresin an excellent coloring agent for the food industry. The commercial quality of the product lies primarily in its coloring capacity, which depends on the carotenoid concentration. Qualitative composition of the oleoresin is also important, because a greater proportion of capsanthin gives it a stronger red coloring capacity. A high proportion of β -carotene and β -cryptoxanthin represents an added value as a source of provitamin A (Mínguez-Mosquera and Hornero-Méndez, 1997). All of the physical, chemical, nutritional, and pharmacological properties of the carotenoid pigments are due to their conjugated diene structure. The destruction of the polyene structure results in the loss of all of these properties, with the destructive reaction being termed decoloration, degradation, or antioxidant activity (Isler, 1971; Goodwin, 1976).

The main negative attribute in the oleoresin is the possibility of pungency. As all of the lipophilic compounds are dissolved in the oil, they are more concentrated than in the raw material, so that fruits that appear nonpungent can produce oleoresins too pungent for use as colorants. This is the aspect that has been most studied to date, with regard to analytical methods, from the point of view of the creation of nonpungent fruit varieties and with the goal of developing techniques for removal of the pungent components (Jinpin et al., 1994; Rajpoot and Govindarajan, 1981; Govindarajan et al., 1977).

After oleoresins suitable for consumption have been obtained, the next problem is to maintain the chromatic quality over time. In industry, the pigment concentrate batch is not used immediately or completely. It is normally employed within a production process, with stock being taken gradually from storage until it is used up. Thus, the oleoresin may be in use for a long time after the date on which it was obtained.

In a product for which the quality depends on the carotenoid content, the ability to predict deterioration in these pigments is crucial. Losses during storage lower the value of the product (Mínguez-Mosquera et al., 1993). Losses during industrial use require constantly corrected formulations to keep the quality uniform (Mínguez-Mosquera et al., 1994). The ability to know how much color of an oleoresin will last after storage or treatment is desirable, so that one is at least able to guarantee its quality for use within a certain time.

The study of oleoresin stability must be approached kinetically and thermodynamically if the results are to be of general use. Color loss in the oleoresin is due to degradation of the carotenoids, and it has been established in model systems that carotenoids are degraded in a compensated set of reactions (Mínguez-Mosquera and Jarén-Galán, 1995; Jarén-Galán and Mínguez-Mosquera, 1997). Although oleoresin is a complex

* Author to whom correspondence should be addressed (telephone 34-954-691054; fax 34-954-691262; e-mail majaren@cica.es).

mixture of different carotenoids in oil, the decoloration reaction can be studied using a simple approach (Labuza, 1981). The whole carotenoid content disappears following a specific kinetic model, and each oleoresin has its own kinetic parameters. As the carotenoid composition in oleoresins is qualitatively uniform, all of the kinetic differences must be induced by the reaction medium. This hypothesis necessarily implies that, in each paprika oleoresin, color is lost following one of the multiple isokinetic forms of one unique reaction. Theoretical demonstration of such a hypothesis is interesting, but the derivation of possible practical applications is even more important.

The aim of the present work is to know if carotenoid pigment degradation in a real system can be explained as an isokinetic reaction. If this is the case, it will be possible to establish a simplified method for studying the stability of paprika oleoresins. Each oleoresin will have its individual thermodynamic idiosyncrasy, but the reaction will be formally the same in all cases. To unify both aspects in a single equation will allow us to know how and how much an oleoresin deteriorates with a solid kinetic basis.

MATERIALS AND METHODS

Raw Material. The study was carried out on six commercial paprika oleoresins provided by different industries. All of the oleoresins have the usual aspect of pepper carotenoid pigment solution in the oil of the fruit, although each one has a different pigment concentration due to the variety of fruit used and the oleoresin extraction procedure employed.

Reaction Conditions. Fifteen aliquots per temperature were taken from each oleoresin and placed in inert, heat-resistant airtight flasks, which were completely filled and put into thermostated chambers at 100, 110, and 120 °C. These three temperatures were used to determine the kinetic, thermodynamic, and prediction equations.

Sampling. A sample of each oleoresin was withdrawn at intervals depending on the temperature employed. In general, the intervals were hours during the first stages of the reaction and days toward the end of the experiment.

Reaction Monitoring. The pigment content of each sample was determined by measuring its absorbance at 454 nm. Approximately 0.02 g of oleoresin was weighed exactly in quadruplicate and dissolved in acetone to a final volume of 25 mL. Of this solution, 0.3 mL was placed in a measuring flask, and acetone was added to a final volume of 10 mL for direct spectrophotometric measurement. To keep absorbance measurements within adequate spectrophotometric levels, the weight of sample was increased with the gradual decrease in pigment content taking place during the reaction. The unit of concentration used in the study was the percentage of color retained at 454 nm, which, on having standardized the intermediate dilutions, was calculated from the following expression, where the subscript "i" indicates the sample at a given time and the subscript "0" the initial sample:

$$\% \text{ retention} = \frac{\text{Abs}_i/\text{Pm}_i}{\text{Abs}_0/\text{Pm}_0} \times 100$$

Kinetic and Thermodynamic Calculations. The degradation reaction rate (k_v) was calculated as the percentage of color retained with time in hours (t). Individually, each oleoresin yielded 60 data items at each temperature. The mathematical fit was performed by assuming that the reaction was of zero or first order, obtaining for each order of reaction a total of 18 regression lines for the subsequent determination of thermodynamic parameters. The integrated rate equations expressed as percentage of retention with time are

zero-order reaction

$$\% \text{ retention} = 100 - k_v t \quad (1)$$

first-order reaction

$$\% \text{ retention} = 100/e^{k_v t} \quad (2)$$

The thermodynamic study of each oleoresin was carried out from semilogarithmic correlation of the k_v obtained at each temperature with $1/T$. The increases in activation enthalpy (ΔH) and entropy (ΔS) were obtained using the Planck (h) and Boltzmann (k) constants:

$$k_v = T \frac{k}{h} e^{\Delta S/R} e^{-\Delta H/RT} \Rightarrow \ln \frac{k_v}{T} = \ln \frac{k}{h} + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (3)$$

As neither order of reaction was dominant, the pair of thermodynamic values for the two was determined for each oleoresin, yielding six thermodynamic equations for each order of reaction.

The pairs of thermodynamic values obtained were linearly correlated in accord with eq 4, yielding the Gibbs free energy of the reaction (ΔG_{isok}) for the isokinetic temperature of reaction (T_{isok}), giving a final total of two isokinetic equations.

$$\Delta G_{\text{isok}} = \Delta H - T_{\text{isok}} \Delta S \Rightarrow \Delta H = T_{\text{isok}} \Delta S + \Delta G_{\text{isok}} \quad (4)$$

RESULTS

Characteristics of the Raw Material. The raw materials were oleoresins of very different qualities, compositions, and physical characteristics. The oleoresins were identified numerically without hierarchical implication. Of the initial differences, the most notable were that the pigment concentration of oleoresins O1, O4, and O6 was double that of oleoresins O2 and O3 and that the oleoresin O5 pigment concentration was less than half that of oleoresins O2 or O3. Physically, there were also great differences: oleoresin O5 was very liquid, whereas oleoresin O6 was pasty; oleoresins O1 and O4 were apparently liquids, although with small lumps at low temperature.

Kinetics of Color Degradation in the Oleoresins. Tables 1 and 2 show the kinetic parameters of the degradation reactions for the six oleoresins at the three temperatures studied. The equations employed to calculate the rate constants are formulated for a degradation reaction, so in both tables the kinetic parameters appear as absolute values.

Table 1 presents a degradation of zero-order kinetics and Table 2 of first-order. In both cases, the correlations are good. Considering only the correlation coefficient, there seems to be a better linear fit for the straight lines calculated from first-order kinetics, although the differences are not enough to determine a particular order of reaction.

For the two reaction orders and the three temperatures considered, the sequence for the rate constants of oleoresins is approximately

$$O5 \ll O2 \cong O3 < O1 \cong O4 \cong O6$$

This sequence is strictly qualitative and does not reflect quantitative aspects. It can be seen that at 100 °C, oleoresin O4 loses 10% of pigments during the same time that O5 loses 20%, and thus it can be said that oleoresin O4 is much more stable than O5. However, at 120 °C, while oleoresin O4 loses 10%, O5 loses only 15%, so O4 is more stable than O5. This sequence can change with temperature. At 100 °C, the rate constant for the

Table 1. Kinetic Parameters of Oleoresin Degradation in Zero-Order Reaction

	rate constant (k_v)	ordinate	R
Temperature = 100 °C			
oleoresin 1	0.06355 ± 0.00321	99.67 ± 1.13	0.9707
oleoresin 2	0.08591 ± 0.00428	93.94 ± 1.54	0.9732
oleoresin 3	0.08618 ± 0.00321	97.72 ± 1.15	0.9843
oleoresin 4	0.06015 ± 0.00236	95.24 ± 0.83	0.9809
oleoresin 5	0.11398 ± 0.00800	83.13 ± 2.84	0.9447
oleoresin 6	0.05970 ± 0.00299	98.29 ± 1.04	0.9740
Temperature 110 = °C			
oleoresin 1	0.08803 ± 0.007593	93.64 ± 1.83	0.9097
oleoresin 2	0.14255 ± 0.009025	90.47 ± 2.18	0.9482
oleoresin 3	0.13098 ± 0.008070	92.95 ± 2.00	0.9539
oleoresin 4	0.07704 ± 0.007056	92.23 ± 1.70	0.8998
oleoresin 5	0.20386 ± 0.016480	105.75 ± 3.35	0.9244
oleoresin 6	0.08032 ± 0.008681	95.45 ± 2.09	0.8680
Temperature 120 = °C			
oleoresin 1	0.14387 ± 0.00704	91.86 ± 1.27	0.9680
oleoresin 2	0.19760 ± 0.00962	88.57 ± 1.74	0.9683
oleoresin 3	0.17540 ± 0.01040	87.41 ± 1.88	0.9539
oleoresin 4	0.14655 ± 0.00853	91.47 ± 1.54	0.9556
oleoresin 5	0.20873 ± 0.02340	78.30 ± 3.30	0.8761
oleoresin 6	0.14135 ± 0.00939	90.54 ± 1.70	0.9433

Table 2. Kinetic Parameters of Oleoresin Degradation in First-Order Reaction

	rate constant (k_v)	ordinate	R
Temperature 100 = °C			
oleoresin 1	0.00083 ± 0.00004	4.6182 ± 0.0159	0.9674
oleoresin 2	0.00134 ± 0.00004	4.5762 ± 0.0155	0.9883
oleoresin 3	0.00129 ± 0.00003	4.6184 ± 0.0118	0.9936
oleoresin 4	0.00080 ± 0.00002	4.5690 ± 0.0077	0.9910
oleoresin 5	0.00275 ± 0.00007	4.5228 ± 0.0247	0.9923
oleoresin 6	0.00077 ± 0.00003	4.6013 ± 0.0109	0.9825
Temperature 110 = °C			
oleoresin 1	0.00122 ± 0.00009	4.5465 ± 0.0225	0.9269
oleoresin 2	0.00277 ± 0.00009	4.5573 ± 0.0223	0.9848
oleoresin 3	0.00233 ± 0.00011	4.5737 ± 0.0295	0.9678
oleoresin 4	0.00108 ± 0.00009	4.5340 ± 0.0236	0.9025
oleoresin 5	0.00367 ± 0.00016	4.7313 ± 0.0332	0.9752
oleoresin 6	0.00109 ± 0.00011	4.5674 ± 0.0275	0.8759
Temperature 120 = °C			
oleoresin 1	0.00220 ± 0.00007	4.5446 ± 0.0128	0.9858
oleoresin 2	0.00407 ± 0.00012	4.5564 ± 0.0225	0.9872
oleoresin 3	0.00329 ± 0.00012	4.5234 ± 0.0221	0.9813
oleoresin 4	0.00224 ± 0.00010	4.5420 ± 0.0187	0.9715
oleoresin 5	0.00431 ± 0.00027	4.1947 ± 0.0389	0.9540
oleoresin 6	0.00213 ± 0.00009	4.5228 ± 0.0175	0.9723

decoloration of oleoresin O4 is lower than that for O1, whereas at 120 °C, the order is reversed. Using the term stability, it should be said that oleoresin O4 is more stable than O1 at 100 °C but less stable at 120 °C.

From the point of view of the stability, it is expected that the order obtained under specific conditions will be always maintained, under any experimental conditions, but the results show that two different oleoresins can be more or less similar in stability depending on the temperature at which they are compared. Stability is commonly considered as an absolute property, but it depends qualitatively and quantitatively on temperature. Kinetically, stability is completely analogous to the rate constant and thus subject to the same restrictions. Only with a rigorous thermodynamic study can stability be reduced to a single parameter depending exclusively on the sample.

Thermodynamic Study of the Decoloration Reaction in Oleoresins. Tables 3 and 4 show the values of activation enthalpy and entropy for the degradation reaction of each oleoresin, assuming zero- and first-order

Table 3. Thermodynamic Parameters of Oleoresin Degradation Reaction of Zero-Order Kinetics

	activation enthalpy, kJ/mol	activation entropy, J/mol·K	R
oleoresin 1	-46.342 ± 6.519	-76.889 ± 17.033	0.9902
oleoresin 2	-47.488 ± 5.565	-70.856 ± 14.539	0.9932
oleoresin 3	-40.032 ± 3.807	-90.881 ± 9.920	0.9955
oleoresin 4	-50.677 ± 14.652	-66.028 ± 38.304	0.9606
oleoresin 5	-33.849 ± 19.020	-104.558 ± 49.693	0.8718
oleoresin 6	-49.103 ± 10.175	-70.395 ± 26.585	0.9791

Table 4. Thermodynamic Parameters of Oleoresin Degradation Reaction of First-Order Kinetics

	activation enthalpy, kJ/mol	activation entropy, J/mol·K	R
oleoresin 1	-55.894 ± 8.029	-87.274 ± 20.987	0.9898
oleoresin 2	-64.450 ± 10.970	-59.605 ± 28.665	0.9858
oleoresin 3	-53.794 ± 7.795	-88.646 ± 20.368	0.9896
oleoresin 4	-59.103 ± 15.966	-79.278 ± 41.719	0.9653
oleoresin 5	-11.615 ± 4.092	-161.933 ± 10.694	0.9859
oleoresin 6	-58.425 ± 12.205	-81.274 ± 31.890	0.9788

kinetics. The sign of the calculated parameters has only a mathematical meaning and nothing else. The reason is evident: the kinetic study has to be conducted in such a manner that the rate constant will have positive values, to be used for the thermodynamic study, so the sign is mathematically imposed.

Comparison of Tables 3 and 4 indicates that for each oleoresin, the two thermodynamic values are different depending on reaction order considered. For the first order, the activation enthalpy is always 8–12 kJ/mol higher in absolute value than that calculated for the zero order. The activation entropy is also by about ~8 J/mol·K higher when it is calculated following a first-order kinetic model.

Considering independently each reaction order, the values of enthalpy or entropy of all the oleoresins are within a narrow range of values, except in the case of oleoresin O5. These narrow ranges could be explained as a random distribution individual parameters of each oleoresin around an average, which represents all of the oleoresins. This could be very well explained statistically, because the range of confidence of the individual values includes the mean, with the exception of oleoresin O5, which is not represented by this value of activation enthalpy or the activation entropy. To reduce enthalpy or entropy for all of the oleoresins to a single value would simplify things, but it is unacceptable, as it would imply that for each temperature all of the oleoresins had exactly the same rate constant. Experimental evidence proves this is not so.

Therefore, the small variability between the thermodynamic parameters of all the oleoresins cannot be attributed to a scattering around the mean value caused by experimental errors. Each oleoresin has specific thermodynamic coordinates, responsible for its particular kinetic behavior. Although in some cases the two thermodynamic values are numerically similar, they are intrinsic to each oleoresin. Thus, oleoresin O5 is not an exception—it is as different thermodynamically from the other oleoresins as they are from one another.

When the kinetic and thermodynamic equations are grouped in a single expression, eqs 5 and 6 can be readily deduced for theoretical reactions of zero or first order, respectively, and expressed as a function of time (t), temperature (T), and the thermodynamic constants.

zero order

$$\% \text{ retention} = 100 - t T \frac{k}{h} e^{(T\Delta S - \Delta H)/RT} \quad (5)$$

first order

$$\% \text{ retention} = \frac{100}{e^{[tT(k/h)]e^{(T\Delta S - \Delta H)/RT}}} \quad (6)$$

Introduction of the specific thermodynamic parameters of each oleoresin into these equations makes it possible to predict retention for any time and temperature.

The method requires that each oleoresin is treated individually, assuming that decoloration is an independent reaction without thermodynamic similarities between one oleoresin and another. However, the results are not in agreement with the notion that an oleoresin decoloration is due to a loss of conjugation in the double-bond sequence of the respective carotenoids.

This apparent contradiction is common when classical thermodynamics is applied to complex reactions. In principle, the rate constant depends on the temperature and activation entropy and enthalpy, as seen from eqs 5 and 6. In reactions in which the reaction conditions are defined and reproducible, it is assumed that there is a single activation enthalpy defining the reaction and that the terms temperature and entropy represent the environmental conditions under which it takes place. When these concepts are applied to reactions in which the factors external to the reaction cannot be totally controlled and where it is not possible to reproduce the environment in which the reaction takes place, deviations from the theoretical model appear, and the thermodynamic study must be considered isokinetically. This phenomenon is widely reported in complex reactions in which the medium can act as a decisive factor (Ramaswamy et al., 1989; Rhim et al., 1989, 1990; Canjura et al., 1991; Mínguez-Mosquera and Jarén-Galán, 1995; Jarén-Galán and Mínguez-Mosquera, 1997).

In brief, the theory of isokinetic or thermodynamically compensated models postulates that modifications in the medium and conditions of reaction affect not only the activation entropy but also the reaction enthalpy (Labuza, 1981). The same reaction taking place under different environmental conditions results in a set of thermodynamic pairs of values defining an isokinetic straight line. This straight line takes in all of the possible thermodynamic coordinates that a reaction might show as a function of the external medium. The slope of the isokinetic straight line gives the isokinetic temperature—that at which the rate constant of the reaction is unique and independent of the medium—and the ordinate at the origin is the increase in Gibbs free energy of all the reactions at the isokinetic temperature (eq 4).

In practical terms, one can assume that as the medium causes changes in both activation entropy and enthalpy of a reaction, the relationship between the two parameters remains constant. Thus, it can be said that if the medium increases the predisposition of the molecules to react (an increase in activation entropy), the energy required for such a reaction decreases (decrease in activation enthalpy). This is not a device to explain unconnected results but a tool (little known theoretically) enabling the application of classical theories (formulated for ideal situations) to real reactions. Many studies now exist on reactions that previously

could not be related thermodynamically, and the respective approaches are much more generally applicable (Galwey, 1977; Labuza, 1981). Nevertheless, there are many points that remain to be addressed regarding the true significance of thermodynamic compensation.

Considering it axiomatic that in all of the oleoresins the decoloration reaction takes place by loss of conjugation in the double-bond sequence of the carotenoids, we find ourselves with a single reaction in which the structure of each carotenoid and the composition and nature of each oleoresin are environmental factors. This allows the reaction to be considered as a thermodynamically compensated system in which the reaction is not defined exclusively by two thermodynamic values but by an isokinetic straight line.

For the orders of reaction considered in the kinetic study, the existence of thermodynamic compensation has been proven. The isokinetic straight lines and the equations are shown in Figure 1. Both cases clearly show thermodynamic compensation.

The existence of a linear relationship between activation entropy and enthalpy of the decoloration reaction in the different oleoresins allows the equations calculating the percentage of retention to be rewritten, making them depend exclusively on time, temperature, and one of the thermodynamic parameters (the other one being automatically fixed). Given that the reaction responds acceptably to kinetic models of both zero and first order, the equations must take this into account. Hence, eq 7 assumes zero order and includes the isokinetic temperature and free energy corresponding to such order of reaction, and eq 8 assumes first order.

zero order

$$\% \text{ retention} = 100 - t T \frac{k}{h} e^{\Delta S(T - 428.93) - 78.781/RT} \quad (7)$$

first order

$$\% \text{ retention} = \frac{100}{e^{tT \frac{k}{h} e^{\Delta S(T - 406.37) - 90.338/RT}}} \quad (8)$$

Equations 7 and 8 enable the percentage of retention of carotenoids to be predicted for any of the oleoresins under study for any time and temperature, with only the activation entropy of the reaction known.

Application to Decoloration Prediction. To test the reliability of these predictions, the theoretical results calculated were compared with those actually obtained when the samples were subjected to a temperature other than that employed in the kinetic study.

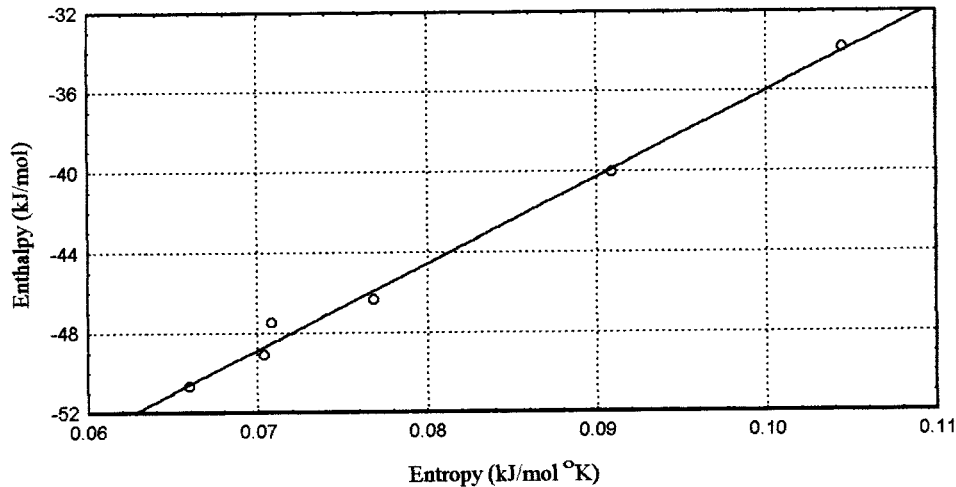
Following the same procedure as described in the section on the kinetic study, series of samples of the six oleoresins were tested at 105 °C. A sample of each oleoresin was taken from the oven periodically, and the percentage of color retained was measured in duplicate. In parallel, using the corresponding activation entropy value of each oleoresin, the theoretical percentage of color that should remain after this period of degradation at the given temperature was calculated by employing kinetic models of both zero order and first order.

Figure 2 shows the actual value of percentage of color retained in each determination during the degradative treatment of the six oleoresins, V_s , the corresponding value obtained theoretically using the prediction equa-

Zero order reaction

$$\text{Enthalpy} = -78.781 + 428.937 \times \text{Entropy}$$

$$R = 0.9956$$

**First order reaction**

$$\text{Enthalpy} = -90.338 + 406.319 \times \text{Entropy}$$

$$R = 0.9969$$

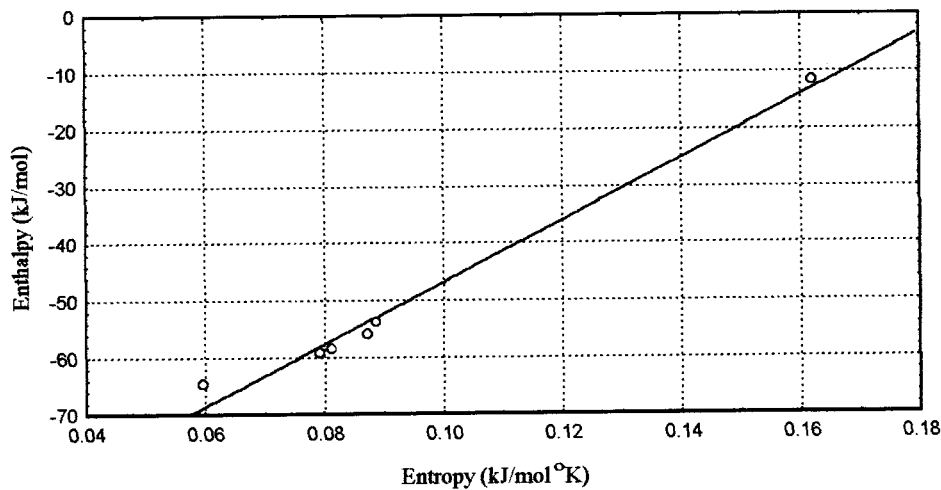


Figure 1. Isokinetic straight lines for the decoloration reaction of paprika oleoresins according to the kinetic models of zero and first order.

tions. Figure 2a includes the calculated values under a zero-order kinetic model and Figure 2b those obtained under first-order kinetic model. A perfect prediction system should give a straight line with a slope of 1. Points placed under this line mean that the retention predicted is lower than the retention measured, whereas points above the line mean a higher predicted retention than the measured one. Drawing lines to fix an interval where the differences between the retention measured and calculated were <15%, it can be seen that the prediction equation obtained with the first-order kinetic model is more accurate than that calculated for zero-order. More than 90% of the predictions done with the equation calculated using the first-order kinetic model are within the range of error lower than 15% and scattered around the line of slope 1. There are no tendencies in the prediction error, and this is proportionally similar along the reaction. It can be concluded

that both kinetic models are acceptable for decoloration prediction, although reliability is higher with the first-order model.

Possible Extrapolation of the Isokinetic Model.

This method can speed up the calculations for the prediction of the color retained in any of the oleoresins studied, so that the stability can be cataloged. However, the overriding practical use of the present study is its extrapolation to any type of paprika oleoresin. For this, at least one of the thermodynamic parameters of the oleoresin must be known before the prediction equations can be used. Such a parameter can be found by determining the activation entropy in the decoloration reaction experimentally combining several treatments at different times and temperatures and obtaining the paired value of activation enthalpy. In practical terms, compensation will be reduced to a purely formal aspect of the reaction without impact on experimental ap-

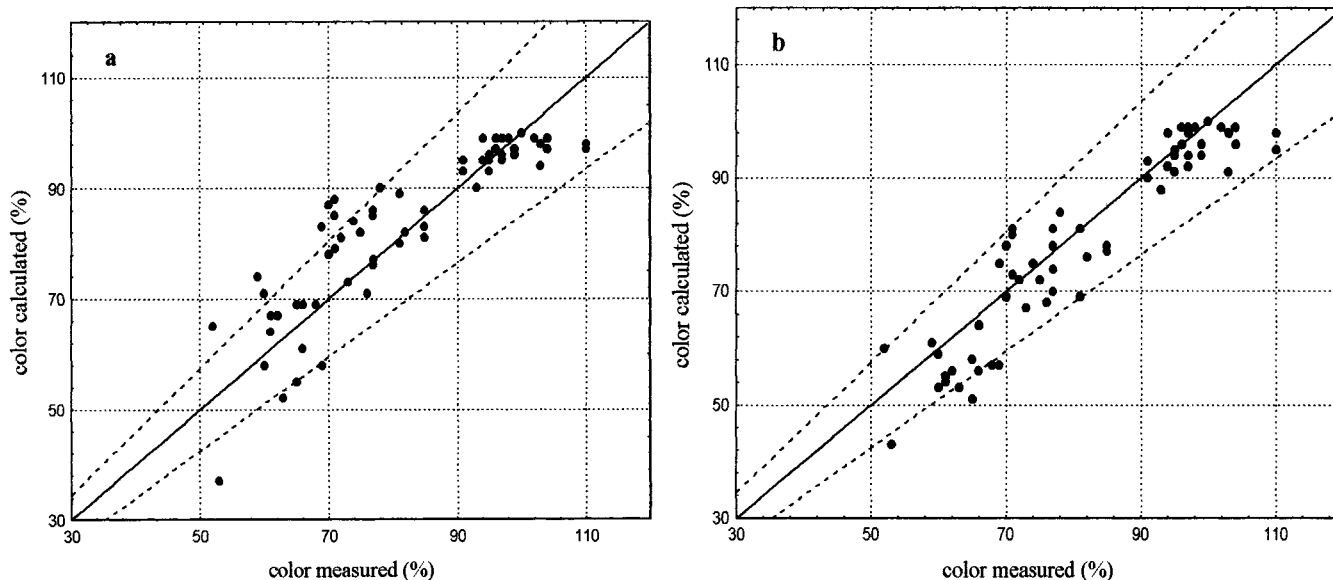


Figure 2. Color retention measured versus color retention predicted during a degradative treatment of six oleoresins at 105 °C. Prediction done using both equations calculated under zero- (a) and first-order (b) kinetic models. (Solid line) error in the prediction is 0% with respect to the color retention measured; (dashed line) error in the prediction is 15% with respect to the color retention measured.

proach or determination of the reaction parameters. There is also a second possibility, with very attractive perspectives. Assuming that the unifying approach is correct and that all of the oleoresins are degraded in agreement with thermodynamic coordinates included on a single isokinetic straight line, the problem with each individual sample is to know its topographic location on that line. The present study shows that the percentage of retention at a given time and temperature depends only on the activation entropy of the oleoresin. This approach can be applied in reverse—from a knowledge of the percentage of retention at a given time and temperature, the activation entropy of an oleoresin included on the straight line can be deduced. Using this approach, eqs 9 and 10 (obtained for theoretical kinetics of zero and first order) can be deduced mathematically.

zero order

$$\Delta S = \frac{RT \left[\ln(100 - \%Ret) - \ln \left(t T \frac{K}{h} \right) \right] - Ord_{isok}}{T - T_{isok}} \quad (9)$$

first order

$$\Delta S = \frac{RT \left[\ln[\ln(100 - \%Ret)] - \ln \left(t T \frac{K}{h} \right) \right] - Ord_{isok}}{T - T_{isok}} \quad (10)$$

If this hypothesis is verified, simplification will be maximized. The conclusion could be summarized as follows: in a compensated system, any sample could be localized with a simple analysis at known time and temperature. Such an approach is valid in theory, but more oleoresins will have to be studied to prove that all are really included in the scheme of a single, thermodynamically compensated reaction. In principle, the theory has been derived from a study carried out on paprika oleoresins, but both the theory and the

equations could be valid and extrapolated to any reaction involving thermodynamic compensation.

LITERATURE CITED

- Attuquayefio, V. K.; Buckle, K. A. Rapid sample preparation method for HPLC analysis of capsaicinoids in capsicum fruits and oleoresins. *J. Agric. Food Chem.* **1987**, *35*, 777–779.
- Canjura, F. L.; Schwartz, S. J.; Nunes, R. V. Degradation kinetics of chlorophylls and chlorophyllides. *J. Food Sci.* **1991**, *56*, 1639–1643.
- Cortijo, M.; Fuster, A.; Martínez, E. An infrared study of red pepper paprikas and their oleoresins. *An. Quim.* **1982**, *78*, 69–71.
- Galwey, A. K. Compensation effect in heterogeneous catalysis. *Adv. Catal.* **1977**, *26*, 247–322.
- Goodwin, T. W. Distribution of carotenoids. In *Chemistry and Biochemistry of Plant Pigments*; Goodwin, T. W., Ed.; Academic Press: New York, 1976; Vol. 1.
- Govindarajan, V. S.; Narasimhan, S.; Dhanaraj, S. Evaluation of spices and oleoresins. II. Pungency of capsicum by Scoville Heat Units. A standardized procedure. *J. Food Sci. Technol.* **1977**, *14*, 28–34.
- Isler, O. *Carotenoids*; Isler, O., Ed.; Birkhäuser Verlag: Basel, 1971.
- Jarén-Galán, M.; Mínguez-Mosquera, M. I. β -carotene and capsanthin co-oxidation by lipoxygenase. Kinetic and thermodynamic aspects of the reaction. *J. Agric. Food Chem.* **1997**, *45*, 4814–4820.
- Jinpin, Y.; Nair, M. G.; Chandra, A. Supercritical carbon dioxide extraction of Scotch Bonnet (*Capsicum annuum*) and quantification of capsaicin and dihydrocapsaicin. *J. Agric. Food Chem.* **1994**, *42*, 1303–1305.
- Labuza, T. P. Enthalpy/Entropy compensation in food reactions. *Food Technol.* **1981**, *34*, 67–77.
- Mínguez-Mosquera, M. I.; Hornero-Méndez, D. Changes in provitamin A during paprika processing. *J. Food Prot.* **1997**, *60*, 853–857.
- Mínguez-Mosquera, M. I.; Jarén-Galán, M. Kinetics of the decoloring of carotenoid pigments. *J. Sci. Food Agric.* **1995**, *67*, 153–161.
- Mínguez-Mosquera, M. I.; Jarén-Galán, M.; Garrido-Fernández, J. Effect of processing of paprika on the main carotenes and esterified xanthophylls present in the fresh fruit. *J. Agric. Food Chem.* **1993**, *41*, 2120–2124.

- Mínguez-Mosquera, M. I.; Jarén-Galán, M.; Garrido-Fernández, J. Influence of the industrial drying processes of peppers for paprika on the carotenoid content. *J. Agric. Food Chem.* **1994**, *42*, 1190–1193.
- Rajpoot, N. C.; Govindarajan, V. S. Paper chromatographic determination of total capsaicinoids in capsicums and their oleoresins with precision, reproducibility, and validation through correlation with pungency in Scoville Units. *J. Assoc. Off. Anal. Chem.* **1981**, *64*, 311–318.
- Ramaswamy, H. S.; van de Voort, F. R.; Ghazala. An analysis of TDT and Arrhenius methods for handling process and kinetic data. *J. Food Sci.* **1989**, *54*, 1322–1326.
- Rhim, J. W.; Nunes, R. V.; Jones, V. A.; Swartzel, K. R. Appearance of a kinetic compensation effect in the acid-catalyzed hydrolysis of disaccharides. *J. Food Sci.* **1989**, *54*, 222–223.
- Rhim, J. W.; Jones, V. A.; Swartzel, K. R. Kinetic compensation effect in the heat denaturation of whey protein. *J. Food Sci.* **1990**, *55*, 589–592.

Received for review July 21, 1998. Revised manuscript received November 30, 1998. Accepted December 1, 1998. We express our sincere gratitude to CICYT of the Spanish Government for supporting this research under the project ALI97-0352.

JF9807972