Use of a Pressuremeter To Measure the Kinetics of Carbon Dioxide Evolution in Chemically Leavened Wheat Flour Dough

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Among a number of impediments to a wider use of chemical leavening agents in bakery applications is the lack of standardized instrumentation capable of providing information on the rates of CO_2 production from chemical leaveners in a format that is meaningful to both the technologist (i.e., the dough rate of reaction or DRR) and the researcher (e.g., in terms of fundamental units—kmol CO_2 per kg of dough per s). This paper presents an original methodology to carry out the DRR test using a commercial pressuremeter, the Gassmart apparatus, and to model the kinetics of CO_2 evolution of chemically leavened dough. Lean formula doughs were leavened at 27 and 39 °C with four chemical leavening systems containing sodium bicarbonate and one of four leavening acids, sodium acid pyrophosphate 40 (SAPP), adipic acid (ADA), potassium acid tartrate (KAT), and glucono-δ-lactone (GDL). Chemical kinetics theory was used to gain an insight into the reaction mechanisms responsible for the evolution of carbon dioxide from the leaveners. A first-order reaction kinetics model was found to be suitable for describing the neutralizing properties of GDL and ADA leavening systems, whereas a first-order reaction kinetics model for irreversible parallel reactions better described the leavening properties of the acidic salts KAT and SAPP.

INTRODUCTION

It is well-established that measurements of gas production and gas retention during leavening of the dough are of great importance to breadmaking, since doughs with good gas production and good gas retention capacities are a prerequisite for making good bread (1). While measurements of a dough's gas retention properties have received a great deal of attention, particularly over the past few years (2−6), actual gas production properties are typically not measured, even though this information is required to model such important breadmaking phenomena as bubble growth during proving of the dough (7). In a recent study, Chiotellis and Campbell (7) noted that a technique capable of providing accurate information on the rates of carbon dioxide production in fermenting dough is still needed.

While fermentation of bread dough is traditionally carried out by the action of yeast cells on fermentable sugars, bread dough can also be leavened using chemical agents alone or in combination with the yeast (8, 9). These chemical leavening agents are particularly useful for leavening bread dough during unconventional processing, such as extrusion processing (10, 11), for doughs that are subject to refrigerated or frozen storage (12−16), or for microwave "baking" purposes (11, 17−19). Chemical leavening offers several advantages over biological (yeast) leavening. For example, prolonged refrigeration or frozen storage does not affect carbon dioxide production capabilities in doughs prepared with chemical leaveners. Also, by judicious selection of chemical leaveners, doughs are capable of producing carbon dioxide at working temperatures that span from ambient to baking temperatures (8), shortening proofing times and hence preparation time in the bakery (20).

In the baking industry, the rate of reaction of chemical leavening systems is typically measured in terms of the dough rate of reaction (DRR) (8, 21), an empirical test that measures the percentage of gaseous carbon dioxide evolved as a function of time. Because of their simplicity, pressuremeters have also been used to evaluate gas production in yeasted dough (22, 23) and in chemically leavened dough (24), with results typically shown as a pressure vs time plot. However, such a plot does not directly characterize the chemical leavening system in terms of the DRR test nor can the results be easily interpreted using chemical kinetics theory.

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Gas production in chemically leavened products is defined by a chemical neutralization reaction whereby sodium bicarbonate, the preferred source of carbon dioxide (*8*, *25*), reacts with a leavening acid to evolve carbon dioxide at a specified rate. Conveniently, the chemistry of the reaction is straightforward as the type and quantities of reactants required to ensure neutralization are governed by stoichiometry (*8*, *25*), whereas the rates of carbon dioxide production are governed by chemical kinetics. Although the stoichiometry of the chemical leavening reaction has been recognized (*8*, *26*, *27*), the use of chemical kinetics theory to describe the chemical leavening reactions has not yet been reported.

In a chemically reacting system, many simultaneous chemical processes take place via consecutive or parallel chemical reaction paths, so that the goal of chemical kinetics is to measure and interpret the temporal evolution of these paths, in order that the overall rate of reaction can be described analytically (*28*). In biochemical reactions, numerous parallel and consecutive paths are possible (*28*), so that, for example, an analytical description of carbon dioxide production by yeast fermentation of sugars is extremely complex (*29*). The simplicity of chemical leavening reactions suggests that an analytical description of carbon dioxide production in leavening dough in terms of chemical kinetics principles may be feasible through the use of chemical leaveners. Such a description will permit the identification of not only reactant and byproduct species but also intermediate species, which often vanish during the course of a reaction (*30*). Recognition of the role of intermediate species should provide a more complete description and understanding of the chemical leavening reaction.

Gas production rates in chemical leavening systems depend on the type and concentration of reactants and products, the availability of water, and the reaction temperature and pressure via the laws of chemical kinetics for a chemical neutralization reaction. Therefore, it is theoretically possible to express the properties of chemical leaveners in terms of chemical kinetics parameters (e.g., order of the chemical reaction and reaction rate constant at a given temperature or pressure). The objective of this paper is to use a pressuremeter to characterize the gas production properties of selected chemical leavening systems in wheat flour dough in light of chemical kinetics theory underlying chemical neutralization reactions but also to relate the results to the technologically relevant DRR test.

MATERIALS AND METHODS

Wheat Flour and Chemical Leavening Systems. The straight-grade flour was obtained from a number 1 grade sample of Canadian Western Red Spring wheat milled on the pilot mill of the Canadian International Grains Institute (Winnipeg, MB). Flour protein and ash contents in the flour were 14.0 and 0.45%, respectively (14% moisture basis).

Chemical leavening systems containing sodium bicarbonate and one of four leavening acids [sodium acid pyrophosphate 40 (SAPP), adipic acid (ADA), potassium acid tartrate (KAT), and glucono-δ-lactone (GDL)] were used. Dough formulations are described in **Table 1**. Water added to the formula was equivalent to Farinograph water absorption minus 2%. Formula ingredients (except the flour) were accurately weighed to the nearest 0.0001 g. Ingredient suppliers were Sigma Aldrich Co. (St. Louis, MO) for sodium chloride and sodium bicarbonate, Aldrich Chemical Co. Inc. (Milwaukee, WI) for SAPP 40 and KAT, and Acatris (Oakville, ON) for GDL.

Measurements of Gas Evolution. Gas production was measured using the Gassmart apparatus (National Manufacturing Division/ TMCO Inc., Lincoln, NE), comprised of six 250 mL aluminum pressure vessels connected to a PC running proprietary data acquisition and analysis software (Gassmart software version 3.31). Data analysis was accomplished in an Excel compatible software

Table 1. Formulation[a,b] Employed to Prepare Experimental Dough Samples

ingredients	SAPP (HL)	ADA (LL)	ADA (HL)	KAT (ML)	GDL (LL)	GDL (HL)
wheat flour	10 g	10 g	10 g	10 g	10 g	10 g
water	67.4%	67.4%	67.4%	67.4%	67.4%	67.4%
sodium chloride	0.75%	0.75%	0.75%	0.75%	0.75%	0.75%
sodium bicarbonate	4.20%	1.40%	4.20%	2.80%	1.40%	4.20%
SAPP	5.83%					
ADA		1.22%	3.65%			
KAT				6.22%		
GDL					3.11%	9.33%

[a] Ingredient amounts expressed on percent flour basis (14% m.b.). [b] Labels in columns reflect leavening acid in the formula with letters in parentheses denoting the concentration of sodium bicarbonate (fwb): LL, low level (1.40%); ML, medium level (2.80%); and HL, high level (4.20%).

(Origin 7.5 Scientific software, Originlab, Northampton, MA) after converting the Gassmart data files (.MXG) into comma delimited files using CSV Builder (RAR Software Systems Inc., Winnipeg, MB). A circulating water bath maintained the pressure vessels at a constant temperature of 27 or 39 °C.

The dry ingredients were poured inside a randomly assigned pressure vessel and blended using a stirring rod with a paddle-shaped end. The formula water, preheated to the desired experimental temperature, was added to the dry ingredients and quickly but gently mixed (less than 40 s) to form a homogeneous mixture using the stirring rod. The gas vessel was then sealed and immersed in the water bath, and its pressure (manometric) was brought to 0 kPa using the gas release valve on the vessel lid. The time interval between the addition of water and the first pressure reading was carefully controlled and kept constant at 55 ± 5 s. The gas pressure exerted by the evolved CO_2 was measured for 150 min at a frequency of 5 readings per second (the pressure transducer sensitivity was better than 10 Pa).

To ascertain the pressure exerted by the CO_2 generated by the chemical leavening system alone, a baseline pressure was measured to correct for the pressure contributions of nonleavening gases, such as water vapor. For each leavening system, the baseline pressure was measured using identical ingredients, except that sodium bicarbonate was excluded to eliminate the source of CO_2. This time-dependent baseline pressure was subtracted from the total gauge pressure. All experiments were carried out in duplicate.

Statistical Analysis. The nonlinear curve fit function of Origin software (Micrococal Origin 7.5, Originlab Corp.) was used to fit an assumed distribution (e.g., theoretical kinetic model) to the experimental data. The Levenberg–Marquardt method was used to minimize the χ^2 statistic (the sum of squares of the deviations of the predicted values from the experimental data, relative to the predicted values) so that a best-fit model could be obtained. Whenever the coefficient of determination of the best-fit model is provided is because, at a 5% level of significance, discrepancies between observed data and predicted values were too small to be due to chance (i.e., the model provided a good fit to the observed data).

RESULTS AND DISCUSSION

DRR. A chemical leavening system evolves carbon dioxide that either escapes the dough in the gaseous state or remains dissolved in the dough. Thus, the total amount of carbon dioxide produced by the chemical leavening system, n, is the sum of the amount of gaseous carbon dioxide, n_1, and the amount of dissolved carbon dioxide, n_2. To evaluate the amount of gaseous carbon dioxide evolved from the chemical leavening reaction, $n_1(t)$, the measured pressure readings arising from the gaseous carbon dioxide were converted into the amount of carbon dioxide using the ideal gas law:

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$$P(t)V = n_1(t)RT$$

$$n_1(t) = P(t)VR^{-1}T^{-1} \tag{1}$$

Here $P(t)$ stands for the pressure exerted by the gaseous CO_2 as a function of time (Pa), V is the volume of the gas vessel (2.5×10^{-4} m³), $n_1(t)$ is the number of moles of gaseous CO_2 evolved as a function of time (mol), R is the universal gas constant (8.315 J mol⁻¹ K⁻¹), and T is the temperature (K). To derive $n(t)$, the moles of evolved carbon dioxide as a function of time, the amount of CO_2 dissolved in the dough, $n_2(t)$, must be determined via the concentration of CO_2 that can be dissolved in the dough, C_M. This concentration was calculated from pressure measurements at long times using Henry's law:

$$C_M = P_f \times H^{-1} \tag{2}$$

where P_f is the partial pressure of CO_2 in the vessel at long fermentation times and H is Henry's law constant (J mol⁻¹). Because $C_M = n_2(\infty)/$(volume of nonaerated part of the dough) $= n_2(\infty)/(m_{dough} \times \rho_{dough}^{-1})$, then experimentally:

$$n_2(\infty) = P_f \times H^{-1} \times m_{dough} \times \rho_{dough}^{-1} \tag{3}$$

where m_{dough} is the mass of dough (kg) and ρ_{dough} is the density of the gas-free dough (assumed to be 1285 kg m⁻³ for all doughs; *31*). Henry's law constant (J mol⁻¹) for carbon dioxide in dough was taken to be equal to $60 \times (T - 273) + 900$ (*32, 33*), where T is the temperature (K). These authors (*32, 33*) took the single experimental value that had been measured in dough at 27 °C earlier (*34*) and made an adjustment for the effect of temperature on the magnitude of H using a linear equation, which for a carbon dioxide-in-water system and the temperature range of 27–39 °C can be considered a realistic assumption (*35, 36*). For any given leavening system, the pressure measured at 150 min was taken as the equilibrium pressure since it was very close (>98%) to the pressure estimated by the fits at time 10^{34} s (i.e., this time corresponds to infinity in numerical simulation software such as ABAQUS).

Because chemical leavening systems do not require an induction time as yeast does (*34, 37*), the experimental chemically leavened doughs attained saturation almost immediately (*32, 33*). After saturation was attained, the number of moles of CO_2 dissolved in the dough would change with time, due to the change in CO_2 solubility brought about by changes in the headspace pressure. However, additional CO_2 that is evolved after saturation is attained mainly progresses to the gaseous state, with n_2 accounting for less than 0.04% of the CO_2 produced during this period in our experimental systems. As a result, the number of moles of CO_2 dissolved in the dough was essentially a time-invariant constant, so that $n_2(\infty) = n_2$. Accordingly, the total number of moles, $n(t)$, evolved by a chemical leavening system at any given time t was given by:

$$n(t) = n_1(t) + n_2 \tag{4}$$

From the 12 sets of experimental pressure readings and eqs 1 and 3, 12 sets of values for n as a function of time could be obtained and interpreted using eq 4.

In technological terms, a chemical leavening system's DRR with time, DRR(t), can be defined by the values of $n(t)$ in eq 4 through:

$$DRR(t) = n(t)/n_{total} \times 100\% \tag{5}$$

where n_{total} is the amount of carbon dioxide included in the formula (mol). The number of moles of carbon dioxide available
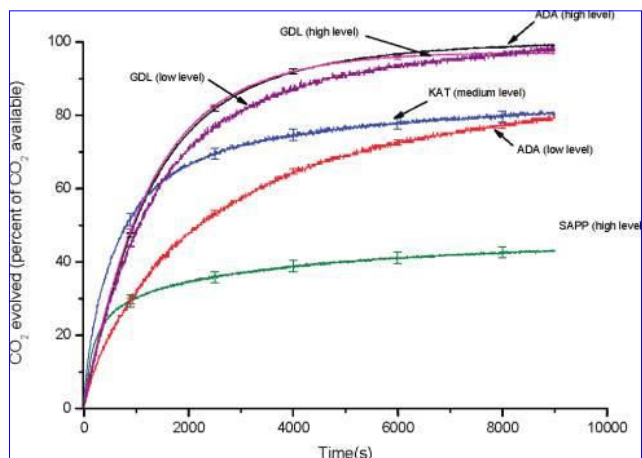

Figure 1. Evolution of carbon dioxide at 27 °C in undeveloped wheat flour doughs that had been prepared with various chemical leavening systems as detected by the Gassmart apparatus. Chemical leavening systems consisted of one leavening acid (SAPP 40, GDL, KAT, or ADA) and one of the following levels of sodium bicarbonate (100 g flour basis, 14% w.b.): high level, 4.2%; medium level, 2.8%; and low level, 1.4%. Error bars denote ± 1 SD.
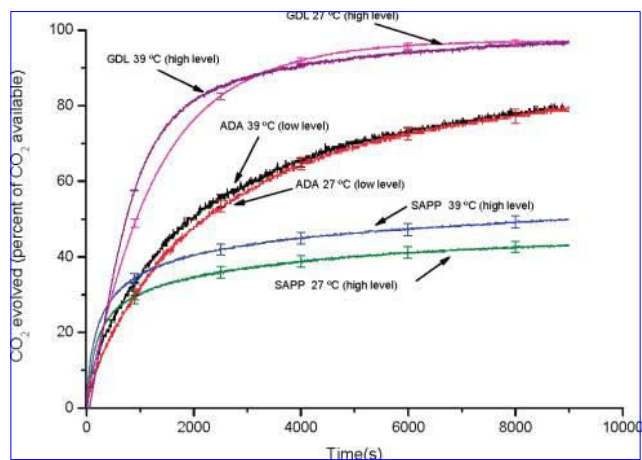

Figure 2. Effect of fermentation temperature on the evolution of carbon dioxide in undeveloped wheat flour doughs that had been prepared with various chemical leavening systems as detected by the Gassmart apparatus. Chemical leavening systems consisted of one leavening acid (SAPP 40, GDL, or ADA) and one of the following levels of sodium bicarbonate (100 g flour basis, 14% w.b.): high level, 4.2%; low level, 1.4%. Error bars denote ± 1 SD.

in the chemical leavening system is equivalent to the number of moles of sodium bicarbonate therein:

$$n_{total} = n_{NaHCO_3} = \frac{m_{NaHCO_3}}{MW_{NaHCO_3}} \tag{6}$$

where n_{NaHCO_3} is the number of moles of sodium bicarbonate, m_{NaHCO_3} is the mass of sodium bicarbonate, and MW_{NaHCO_3} is the molecular weight of sodium bicarbonate (84 g mol⁻¹). In this way, the pressure readings vs time from the Gassmart apparatus can be converted into DRR curves for various chemical leavening systems (**Figure 1**). The effect of temperature on these DRR curves for selected chemical leavening systems is shown in **Figure 2**.

At 27 °C, SAPP 40 was able to evolve about 40% of the available carbon dioxide (**Figure 1**), in agreement with values reported by Heidolph (*8*), Parks et al. (*21*), Conn (*25*), and
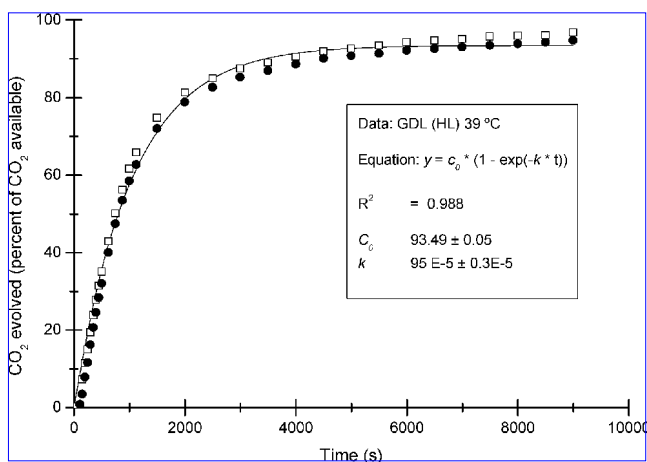
Figure 3. Comparison of experimental data (circles and squares are different duplicates) with a first-order reaction kinetics model (solid line) for the decomposition of GDL (present as D-gluconic acid) into gluconate and hydrogen ions: $C_6H_{12}O_7 \rightarrow C_6H_{10}O_7^- + H^+$. The products of this reaction became the reactants of a much faster reaction: $C_6H_{10}O_7^- + H^+ + NaHCO_3 \rightarrow C_6H_{10}O_7Na + H_2O + CO_2$.

Innophos (*38*) for SAPP 40, although at a slower rate than that reported by these authors. Similarly, KAT evolved about 70% of the available carbon dioxide (**Figure 1**), which was in agreement with the reports of Heidolph (*8*) and Conn (*25*), albeit again at a slower rate. The lack of an agitator in the Gassmart apparatus in contrast to the standard DRR apparatus likely explains the longer reaction times that were observed in this study (**Figures 1** and **2**).

Reaction Kinetics. The reaction between sodium bicarbonate and an acidulant is characterized by the following chemical equation:

$$XH + NaHCO_3 \rightarrow NaX + CO_2(g) + H_2O \qquad (7)$$
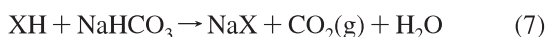
The reaction shown in eq 7, however, only occurs after the acidulant and the sodium bicarbonate dissociate, according to the following general equations:

$$XH \rightarrow X^- + H^+ \text{ or } XH + H_2O \rightarrow X^- + H_3O^+ \qquad (8)$$

$$NaHCO_3 \rightarrow Na^+ + HCO_3^- \qquad (9)$$

If the reaction shown in eq 8 proceeds at a much slower rate than the dissociation in eq 9, then the overall rate of reaction (eq 7) will be determined by the rate of the slow reaction (*30, 39*). Because the sodium bicarbonate dissociates almost immediately upon contact with the formula water, it is the leavening acid's rate of dissociation that is the determinant of the rate of carbon dioxide production (*8, 25*).

If the initial concentration of XH, the leavening acid, is c_0 kmol per m³, and after a time t, c kmol per m³ of XH have decomposed, then integrating the reaction rate with respect to time gives the concentration of the leavening acid, c, at time t as follows:

$$c(t) = c_0 \times (1 - e^{-kt}) \qquad (10)$$

The fitting analysis for this first-order reaction was performed by plotting against time the carbon dioxide production data expressed as a fraction of the original carbon dioxide in the dough system for the two replicates, since $c(t)/c_0$ is equivalent to DRR(t). An example for GDL showing a comparison of experimental data and the model is shown in **Figure 3**, including the associated determination coefficient using the χ^2 test to

Table 2. Parameters and Coefficients of Determination for Curves Fitted to Data on CO_2 Evolved (Percent of Total CO_2 in Dough formula) vs Time ($n = 2$) using Eq 10, As Detected by the Gassmart in Doughs Prepared with One of Two Levels of Sodium Bicarbonate[a] and Fermented at 27 or 39 °C

| | eq[c]: $c = c_0 \times [1 - \exp(-kt)]$ | | |
chemical leavening system[b]	$c_0 \pm$ error	$k \pm$ error $(\times 10^{-4}\ s^{-1})$	R^2
	27 °C		
ADA (LL)	79.77 ± 0.12	5.10 ± 0.03	0.961
ADA (HL)	76.64 ± 0.07	6.50 ± 0.02	0.978
GDL (LL)	94.45 ± 0.04	6.70 ± 0.01	0.995
GDL (HL)	98.30 ± 0.03	7.20 ± 0.01	0.996
	39 °C		
ADA (LL)	79.78 ± 0.12	5.10 ± 0.03	0.961
ADA (HL)	84.06 ± 0.08	7.60 ± 0.03	0.969
GDL (LL)	89.80 ± 0.05	8.20 ± 0.02	0.991
GDL (HL)	93.49 ± 0.05	9.50 ± 0.03	0.988

[a] Sodium bicarbonate concentrations: LL, 1.40 g; and HL, 4.20 g. [b] See **Table 1** for the key on chemical leavening systems. [c] c, percentage of CO_2 evolved (percent of original); t, fermentation time (s).
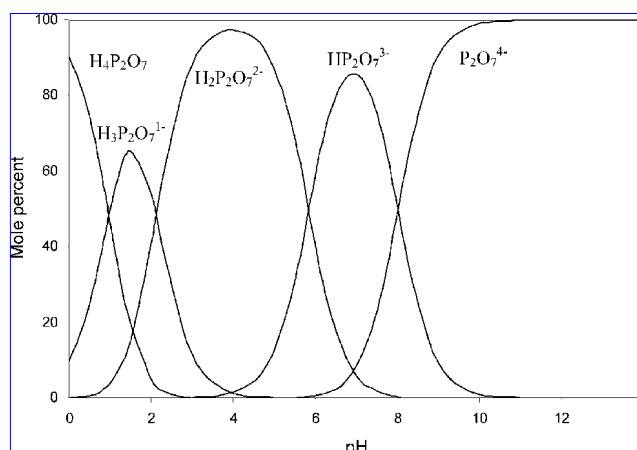

Figure 4. Percent of each of the species of pyrophosphate present in solution as a function of pH at 27 °C. Constructed from the dissociation rate constants and activation energies published by McGilvery and Crowther (*40*) for a pyrophosphoric acid solution kept at 65.5 °C.

minimize the sum of squares of deviations from the mean. The first-order reaction rate model described the observed reaction rates for the GDL and ADA treatments remarkably well, and these results are summarized in **Table 2**. For GDL and ADA, the high determination coefficients (R^2), 99 and 97%, respectively, and the relatively small uncertainty (error) associated with estimating the parameters c_0 and k indicated that the proposed model explained a large percentage of the variation observed for these leavening systems. The fact that the values of the fitting parameters for a given dough system varied with fermentation temperature or concentration of chemical leaveners reflected the sensitivity of the model to these experimental parameters. Regardless of the leavening system, faster reaction kinetics (i.e., higher k) were observed when the fermentation temperature was increased from 27 to 39 °C or when the concentration of sodium bicarbonate was increased from 1.4 to 4.2 g/100 flour. Faster reaction kinetics are expected when the concentration of sodium bicarbonate was increased because this would increase the frequency at which reactant species collide (*30*).

In contrast, the rates of carbon dioxide evolution for the experimental samples containing acidic salts (SAPP and KAT) did not conform to a first-order reaction rate. Therefore, the
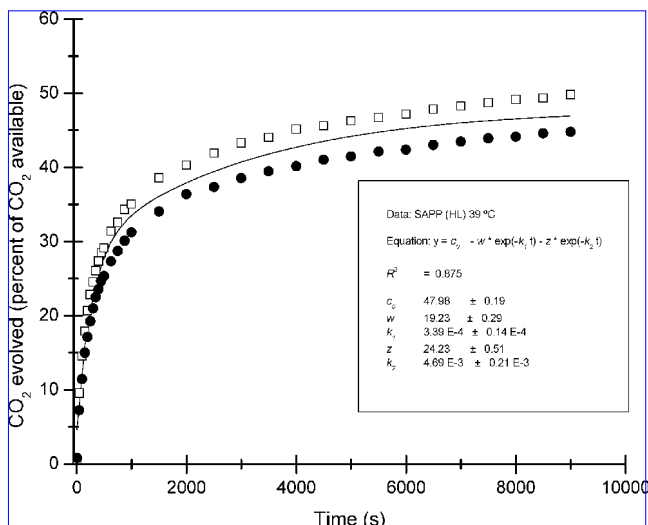
Figure 5. Comparison of experimental data (two duplicates) with a two-step parallel first-order reaction model (solid line) for the decomposition of SAPP into sodium pyrophosphate and hydrogen ions: $Na_2H_2P_2O_7 \rightarrow Na_2P_2O_7^{2-} + 2H^+$ and $Na_2H_2P_2O_7 \rightarrow Na_2HP_2O_7^{1-} + H^+$. The products of these reactions became the reactants of a much faster reaction: $Na_2P_2O_7^{2-} + Na_2HP_2O_7^{1-} + 3H^+ + 3\ NaHCO_3 \rightarrow Na_4P_2O_7 + Na_3HP_2O_7 + 3\ H_2O + 3\ CO_2$.

overall reaction rate for the dissociation of the acidic salts was surmised to be attributable to more than one elementary reaction. Szabó (*39*) specified that parallel reactions may be present in a chemical reaction when a substance forms in more than one way. In such a case, the dissociation of the acidic salt is underlined by two parallel reactions occurring at comparable rates so that the overall chemical neutralization reaction (i.e., the one producing the CO_2 molecule) could not be attributed exclusively to either of the parallel chemical reactions. In such a case, the dissociation of SAPP 40 and KAT involved two elementary steps, one of which may have occurred at a slower rate than the other.

A simple model for parallel reactions involving two steps in which three species, *A*, *B*, and *C*, participated was discussed by Szabó (*39*). His analysis was applicable to parallel reactions where the individual steps followed first-order kinetics and were irreversible with either a mole of *A* or *B* reacting to form 1 mol of *C*:

$$A \xrightarrow{k_1} C \xleftarrow{k_2} B \atop x \qquad c \qquad y \tag{11}$$

where k_1 = the rate constant for the $A \rightarrow C$ reaction, k_2 = the rate constant for the $B \rightarrow C$ reaction, and *x*, *y*, and *c* are the

concentrations in the dough of initial reactants and final products, respectively.

The simultaneous differential equations are

$$-\frac{dx}{dt} = k_1 x \tag{12}$$

$$-\frac{dy}{dt} = k_2 y \tag{13}$$

$$\frac{dc}{dt} = k_1 x + k_2 y \tag{14}$$

The concentration of the final product, *c*, has the form of a second-grade exponential function (*39*):

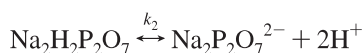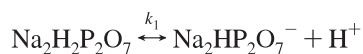$$c(t) = c_0 - we^{-k_1 t} - ze^{-k_2 t} \tag{15}$$

where *w* and *z* are constants. When $t = 0$, $c = 0$, so that $w + z = c_0$, with c_0 thus being equivalent to the initial concentration of the leavening acids SAPP or KAT in the dough. Equation 15 shows that the formation of the hydrogen ion is brought about by a chemical reaction involving two steps that denote the parallel reactions associated with the dissociation of the acid salt to liberate the hydrogen ions. It is worth noting that the model described in eq 15 assumes that when a molecule of *C* is formed, a subsequent (albeit fast) reaction between *C* and the bicarbonate ion (i.e., a rapid neutralization reaction) leads to the formation of CO_2.

To investigate the hypothesis that the dissociation of KAT and SAPP 40 involved parallel reactions, a mechanism involving two hydrogen ion-liberating species is necessary. The influence of pH on the relative proportions of each of the pyrophosphate species that are present in a solution of sodium pyrophosphate is shown in **Figure 4** (*40*). At any given pH, no more than three pyrophosphate species can be present in solution. According to the literature, the pH of dough chemically leavened with SAPP lies between 7.3 and 7.6 (*8, 25, 41*). At a pH range between 7.3 and 7.6 for SAPP dough, **Figure 4** suggests that the following pyrophosphate anionic species are present in solution: $H_2P_2O_7^{2-}$, $HP_2O_7^{3-}$, and $P_2O_7^{4-}$, with the latter two species predominating over this pH range. Hence, it is reasonable to propose that the reaction mechanism of SAPP 40 involved two elementary steps, one of which occurred at a slower rate than the other. The slower rate step would therefore be regarded as the rate-limiting step. These elementary two steps are shown in the following equations:

Table 3. Parameters and Coefficients of Determination of Curves Fitted to Data on CO_2 Evolved (Percent of Initial CO_2) vs Time ($n = 2$) using Eq 15, As Detected by the Gassmart in Doughs Prepared with One of Two Levels of Sodium Bicarbonate[a] and Fermented at 27 or 39 °C

chemical leavening system[b]	$k_1 \pm$ error $(\times 10^{-4}\ s^{-1})$[d]	$k_2 \pm$ error $(\times 10^{-3}\ s^{-1})$[d]	$c_0 \pm$ error[d]	$w \pm$ error[d]	$z \pm$ error[d]	R^2
		eq[c]: $c(t) = c_0 - we^{-k_1 t} - ze^{-k_2 t}$				
		27 °C				
SAPP (HL)	3.25 ± 0.13	3.76 ± 0.16	45.89 ± 0.18	17.85 ± 0.27	24.83 ± 0.56	0.904
KAT (ML)	4.01 ± 0.22	2.22 ± 0.09	84.24 ± 0.26	30.53 ± 1.25	47.68 ± 1.33	0.942
		39 °C				
SAPP (HL)	3.39 ± 0.14	4.69 ± 0.21	47.98 ± 0.19	19.23 ± 0.29	24.23 ± 0.51	0.875
KAT (ML)	4.04 ± 0.26	3.04 ± 0.10	79.57 ± 0.22	19.79 ± 0.78	54.83 ± 0.93	0.912

[a] Sodium bicarbonate concentrations: ML, 2.80 g; and HL, 4.20 g. [b] See **Table 1** for the key on chemical leavening systems. [c] *c*, CO_2 evolved (percent of original); *t*, fermentation time (s). [d] k_1 and k_2 are rate constants (s^{-1}); *w* and *z* are constants so that $w + z = c_0$, with c_0 being the concentration of SAPP or KAT in the dough as defined in the text.

$$Na_2H_2P_2O_7 \overset{k_1}{\leftrightarrow} Na_2HP_2O_7^- + H^+$$

$$Na_2H_2P_2O_7 \overset{k_2}{\leftrightarrow} Na_2P_2O_7^{2-} + 2H^+$$

The exponential function was fitted to the experimental data (duplicates, nonaveraged data), associated with each experimental treatment. **Figure 5** illustrates for SAPP 40 that a second-grade exponential function provided a good fit to the experimental data associated with this acidic salt. A summary of the fitting analysis is shown in **Table 3** for SAPP 40 and KAT. Coefficients of determination were high (>88%), although R^2 is known to increase when additional factors are added to fitting functions. The fact that the experimental data for the decomposition of the acidic salts was well-described by the reaction kinetics for parallel reactions suggested that parallel reactions were indeed important in determining the overall rate of reaction in SAPP 40 and KAT. Given the order of magnitude difference between the rate constants k_1 and k_2 (**Table 3**), the reaction liberating the two hydrogen ions has been assigned the rapid rate of reaction (k_2). The two-step reactions noted above are followed by the rapid neutralization reaction of sodium bicarbonate as follows:

$$Na_2HP_2O_7^- + Na_2P_2O_7^{2-} + 3H^+ +$$
$$3NaHCO_3 \rightarrow Na_4P_2O_7 + Na_3HP_2O_7 + 3CO_2 + 3H_2O$$
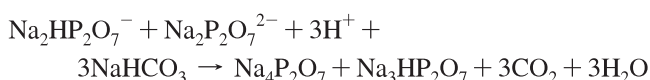
It is further intimated that the CO_2 formed during chemical leavening will cause a drop in pH in the dough (*27*).

Although the data shown in **Table 3** show that the mechanism of reaction of KAT involved two parallel irreversible first-order reactions, there was less certainty in identifying the actual elementary steps responsible for the parallel reactions in KAT. Nonetheless, it is important to note that the reaction mechanism cannot necessarily be predicted from the stoichiometry of the reaction, but it is customarily determined based on the observed experimental kinetics of reaction (*30, 42*). Furthermore, the experimental results indicated that the rate of carbon dioxide production for these two chemical leavening systems increased with fermentation temperature (from 27 to 39 °C), a relationship that was also captured by the rate constants k_1 and k_2, as they also increased with temperature (**Table 3**). This is in agreement with Arrhenius' law, which indicates that the rate of a reaction increases with the temperature, because at higher temperatures the molecules of the reactants move faster and collide more frequently due to their greater kinetic energy. Although the proposed models characterized the reaction rates for SAPP 40 and KAT well, more comprehensive experiments are required to prove the validity of the models in a wider range of experimental conditions as well as to determine the suitability of using kinetic theory for the study of a wider group of chemical leavening systems.

More generally, while the parameters defining the reaction kinetics of the chemical leavening systems studied (**Tables 2** and **3**) have been expressed thus far with respect to DRR curves, conversion of the DRR parameters into fundamental units (e.g., kmol CO_2 per kg of dough per second) can also be accomplished by converting the moles of sodium bicarbonate in eq 5 into per unit mass of dough. Thereby, the time dependence of carbon dioxide production per unit mass of dough for any given temperature can be obtained from the empirical equations shown in **Table 2** and in **Table 3** for ADA and GDL and SAPP and KAT, respectively, after adjusting the units of the pre-

exponential coefficients to account for the usual expression of ingredients on a flour weight basis (fwb). Illustrating for $\bar{c}_0$, the concentration equivalents of CO_2 evolved from the dough in mol of CO_2 per kg of dough due to the chemical neutralization of c_0 mol of ADA or GDL acid.

$$\bar{c}_0 = \frac{c_0 \times \% \, NaHCO_3}{8.4 \times (100 + \% \, water + \% \, NaCl + \% \, NaHCO_3 + \% \, acid)}$$

Similar expressions can be derived for SAPP and KAT.

Furthermore, the rate of carbon dioxide production for ADA and GDL and SAPP and KAT can be obtained by taking the first derivative of $\bar{c}$ with respect to time:

$$\frac{d\bar{c}}{dt} = \frac{d[\bar{c}_0 \times (1 - e^{-kt})]}{dt} = \bar{c}_0 k e^{-kt}$$

or

$$\frac{d\bar{c}}{dt} = \frac{d(\bar{c}_0 - \bar{w}e^{-k_1 t} - \bar{z}e^{-k_2 t})}{dt} = \bar{w}k_1 e^{-k_1 t} + \bar{z}k_2 e^{-k_2 t}$$

The maximum rate of carbon dioxide production is given by the initial slope of the exponential curve (immediately after the onset of fermentation):

$$\left(\frac{d\bar{c}}{dt}\right)_{max} = \bar{c}_0 k$$

or

$$\left(\frac{d\bar{c}}{dt}\right)_{max} = \bar{w}k_1 + \bar{z}k_2$$

For instance, it can be found that the maximum rate of carbon dioxide production in GDL (HL) at 27 °C is 195 μmol CO_2 kg^{-1} s^{-1} and that of SAPP (HL) at 27 °C is 273 μmol CO_2 kg^{-1} s^{-1}. These values are about an order of magnitude larger relative to those reported in yeasted doughs (13 μmol CO_2 kg^{-1} s^{-1}) by Chiotellis and Campbell (*32*).

A new method to carry out the DRR test using the Gassmart apparatus is presented. A first-order reaction kinetics model was found to be suitable for describing the properties of GDL and ADA as leavening systems, whereas a model for first-order reaction kinetics for irreversible parallel reactions better described the leavening properties of the acidic salts KAT (cream of tartar) and SAPP. For the latter, a mechanism for irreversible parallel reactions based on the presence of the two predominant pyrophosphate anionic species in the dough at these pHs ($H_2P_2O_7^{2-}$ and $HP_2O_7^{3-}$) is proposed.

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