

THE BROMATE REACTION IN DOUGH

III. Effect of Continuous Mixing and Flour Particle Size¹

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ABSTRACT

The bromate reaction in a flour-water dough which is continuously mixed under nitrogen can be characterized by a single continuous reaction curve in contrast to the apparent two-phased reaction curve obtained under normal conditions comprising 5 minutes of mixing followed by storage of the dough under controlled conditions. More bromate reacts in the continuously mixed dough than in the normal dough. In the range of potassium bromate concentrations from 0 to 37.50 mg. per kg. of dough (0 to 60 p.p.m. of flour), the reaction in the mixed dough is apparently first-order but the specific rate constant decreases with increasing bromate concentration. At a concentration of 18.75 mg. per kg., the equation for the specific rate constant is

$$k = 1.08 \times 10^4 e^{-11,000/RT} \text{ sec}^{-1}.$$

In the normal dough, the rate of the so-called linear reaction seems to be partially controlled by a physical process. This rate-controlling factor seems to enter into the kinetics of the reaction primarily through the entropy of activation and seems to be related to the accessibility of sulfhydryl groups. The accessibility seems to depend on the specific surface of the flour particles.

This paper, the third of the present series (1,2), compares results of a study of the reaction of the bromate ion in normal flour-water

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doughs with that in doughs which are mixed continuously throughout reaction periods of up to 5 hours, and attempts to explain the differences found in terms of the energy and entropy of activation. It also presents results on the effect of flour particle size which was investigated because it offered possible experimental verification of the hypothesis that continuous mixing increases the physical accessibility of sulfhydryl groups. It is desirable to report the results at this stage of the investigation of the bromate reaction in dough, as they seem pertinent to the setting-up of the mechanism for the reaction as well as having certain practical implications.

Materials and Methods

The flour used for the continuous mixing study was the straight-grade flour described previously (1). This flour has now been in cold storage for one and a half years and consequently the rate of the bromate reaction in a normal, control dough has decreased by about 15% (3).

The flour samples used to study the effect of particle size were specially milled in the Laboratory from a high-grade Canadian hard red spring wheat. The wheat was milled into farina which passed through sieve 30GG and was held on 72GG. A portion of this farina was then reduced to a size which passed through 72GG and was held on 10xx and a second portion was reduced to pass through 10xx (flour). A portion of the flour was further reduced by ball-milling for 16 hours. The protein and ash contents of these flours are given in Table I. The increase in the ash content during ball-milling is attributed to small fragments of ball-mill stones produced during ball-milling. These ash-producing components seem to be inert toward the bromate reaction.

TABLE I
DESCRIPTION OF THE FLOURS OF DIFFERENT PARTICLE SIZE

	PARTICLE SIZE	PROTEIN CONTENT	ASH CONTENT
		% (14% m.b.)	% (14% m.b.)
Farina	Thru 30GG; over 72GG	11.7	0.382
Reduced farina	Thru 72GG; over 10XX	11.7	0.381
Flour	Through 10xx	11.8	0.381
Ball-milled flour		11.6	0.501

The method of analysis for residual bromate ion in dough was described previously (1). In the continuous mixing study, doughs of 60% absorption were mixed under a slightly positive pressure of nitrogen in the GRL mixer (5) throughout reaction periods of up to 5

hours. A change in the mixing rate to 2.57 times the standard rate of 75 r.p.m. of outside pins was obtained by adjustable V-pulleys. To eliminate possible contamination with atmospheric oxygen, a separate dough was mixed for each reaction time. To control the dough temperature at 30°C., the temperature of the circulating water had to be maintained at 29°C. to overcome the heat produced by the mixing. The temperature of the dough was measured with a mercury thermometer immediately after mixing.

In the discussion that follows, the type of dough that was mixed for 5 minutes and then stored under controlled humidity and temperature during the reaction time will be referred to as a normal dough; the other type of dough used in this study will be referred to as a continuously mixed dough.

Results and Discussion

Effect of Continuous Mixing on the Reaction. Figure 1 compares the bromate reaction in a normal dough and in doughs mixed continuously at two different mixing rates for a potassium bromate concentration of 18.75 mg. per kg. of dough. The amount of bromate ion that reacts in a continuously mixed dough is about 50% higher than that in a normal dough. Furthermore, the reaction in the continuously mixed dough can be represented by a smooth curve, whereas in the normal dough the reaction seems to be two-phased over a fairly wide range of experimental conditions (1,2). Similar differences were

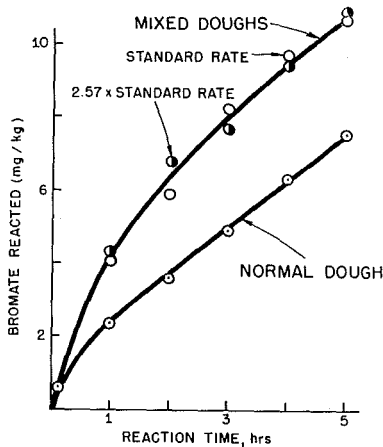


Fig. 1. Reaction of the bromate ion in normal and continuously mixed doughs for initial potassium bromate concentration of 18.75 mg. per kg. of dough.

found at other bromate levels in the range 6.25 to 37.50 mg. per kg. that were investigated.

It can be generalized from the results of Fig. 1 that the linear character of the secondary phase of the bromate reaction in the normal dough arises from the fact that some physical process such as diffusion becomes a major rate-controlling factor when the dough is not being mixed. It seems that this factor can be eliminated almost completely by continuous mixing at the standard rate used in this Laboratory, since no further increase in the bromate reaction was observed when the continuous mixing rate was increased to 2.57 times the standard rate.

In the two subsections that follow, certain features of the effect of continuous mixing will be examined in terms of kinetic and thermodynamic parameters that can be derived from primary data of the type described above. Other aspects of the physical rate-controlling factor will be discussed below when additional experimental data have been presented.

Kinetic Order of the Reaction. Figure 2 gives first-order plots for the data of Fig. 1. In these plots the logarithm of the residual bromate concentration is plotted as a function of reaction time. The results for the high mixing rate are not included in these plots. Both reactions appear to be first order, although the plot for the reaction in the normal dough deviates from linearity when a more expanded ordinate scale is used, and a definite change in slope for the initial and the linear phases is indicated.

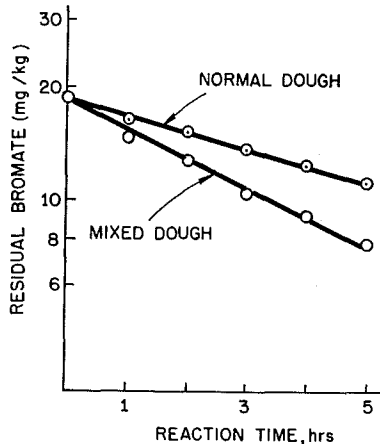


Fig. 2. First-order plots for the reaction of bromate ion in normal and continuously mixed doughs for initial potassium bromate concentration of 18.75 mg. per kg. of dough.

To examine further the first-order character of the bromate reaction in a continuously mixed dough, reaction curves were obtained for a series of potassium bromate concentrations in the range 6.25 to 37.50 mg. per kg. Although the first-order plots of the type shown in Fig. 2 were reasonably linear for all the concentrations used, the specific rate constant decreased slightly with increasing concentrations (see Table II). Accordingly, it seems that the bromate reaction in a continuously mixed dough is not a true first-order reaction and perhaps it might be more correct to refer to it as a *pseudo* first-order reaction.

TABLE II
SPECIFIC RATE CONSTANTS AT VARIOUS POTASSIUM BROMATE CONCENTRATIONS

POTASSIUM BROMATE CONCENTRATION		SPECIFIC RATE CONSTANT $\times 10^5$
<i>mg/kg dough</i>	<i>ppm flour</i>	<i>sec⁻¹</i>
6.25	10	6.47
12.50	20	5.52
18.75	30	4.87
25.00	40	4.45
37.50	60	4.00

It should be emphasized that reference to bromate reaction in either type of dough as being first-order does not imply that the reaction is unimolecular. The combination of the various rate-controlling factors apparently gives a reaction such that when the logarithm of the residual bromate ion concentration is plotted against reaction time a straight line results. This property is sufficient to classify the reaction as having an over-all kinetic order of one. Classification of the so-called linear reaction in a normal dough as first-order needs amplification also. Although under some conditions the reaction curve shows a slight curvature, good straight lines for this part of the reaction in a normal dough have been obtained over a wide range of conditions (1,2). The over-all reaction in a normal dough was divided into a rapid, initial reaction and a slower linear reaction, primarily to emphasize the two-phased nature of the reaction. However, it is quite possible that the linear reaction represents a small segment of an extremely slow first-order reaction.

Activation Energy and Frequency Factor. Figure 3 gives Arrhenius plots for the bromate reactions in normal and continuously mixed doughs for a potassium bromate concentration of 18.75 mg. per kg. The slopes by the method of least squares give 11,600 and 10,160 cal. per mole as the activation energies of the reactions in continuously mixed and normal doughs respectively. The frequency factors, determined from the intercepts of the lines in Fig. 3, are 1.08×10^4

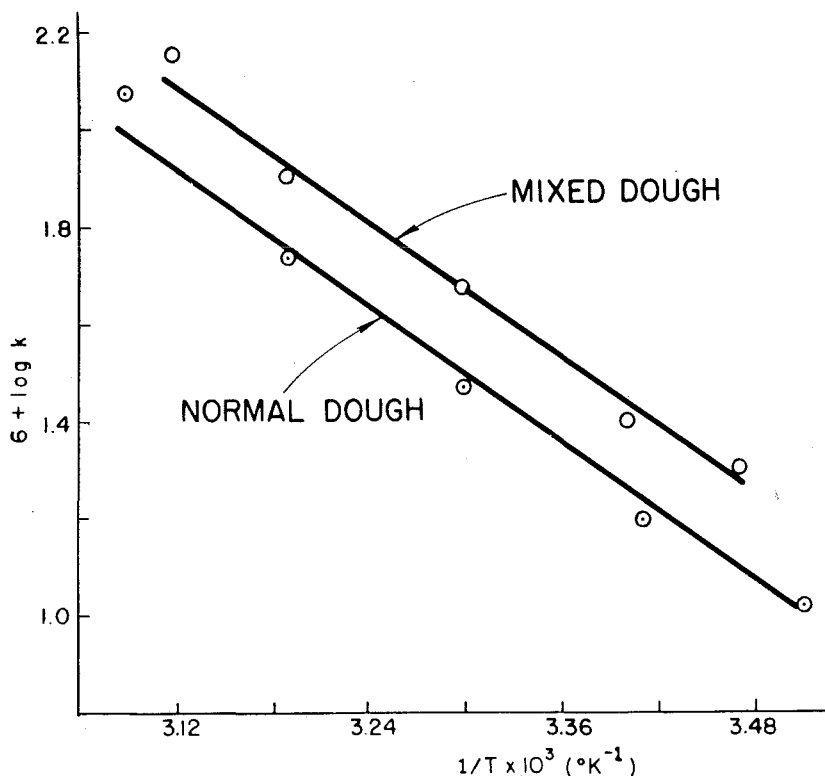


Fig. 3. Arrhenius plots showing the logarithm of the rate constant as a function of the reciprocal of the absolute temperature for bromate reactions in normal and continuously mixed doughs for an initial potassium bromate concentration of 18.75 mg. per kg. of dough.

sec⁻¹ and 0.80×10^4 sec⁻¹ for the reactions in continuously mixed and normal doughs.

If the above values are substituted into the integrated form of the Arrhenius equation

$$k = A e^{-E/RT} \tag{1}$$

where A is the frequency factor and E the activation energy, the rate constants for the concentration of potassium bromate used take on the values:

$$k = 1.08 \times 10^4 e^{-11,600/RT} \text{ sec}^{-1} \tag{2}$$

and

$$k = 0.80 \times 10^4 e^{-10,610/RT} \text{ sec}^{-1} \tag{3}$$

for the reactions in continuously mixed and normal doughs respectively. The same activation energy and frequency factor (con-

verted to proper units) are obtained when the so-called linear reaction in a normal dough is treated according to zero-order kinetics. The activation energy was reported previously (1) and the frequency factor was calculated during the present study using the previous results.

For comparison, the activation energy and the frequency factor were determined for a potassium bromate concentration of 12.50 mg. per kg. in a continuously mixed dough and were found to be 10,800 cal. per mole and $1.07 \times 10^4 \text{ sec}^{-1}$, respectively. The somewhat lower activation energy at the lower bromate concentration offers a possible explanation for the increase in the specific rate constant with decreasing bromate concentration given in Table II.

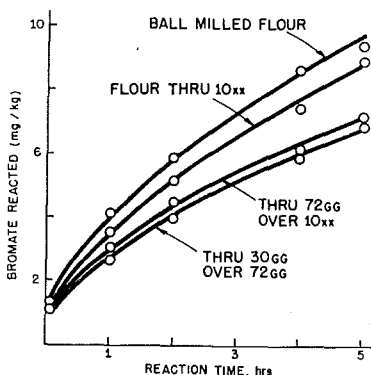


Fig. 4. The bromate reaction at 30°C. in normal doughs prepared from flours of different particle size.

It is possible that the extent to which the physical accessibility factor controls the rate of reaction varies with bromate concentration.

Effect of Flour Particle Size. Figure 4 shows the bromate reaction in normal doughs mixed under nitrogen to 60% absorption from flours which differed only in the size of the particles comprising each sample, with the exception of the ball-milled flour which also had a higher ash content. The initial potassium bromate concentration in this study was 18.75 mg. per kg. of dough. It is seen that the rate of bromate disappearance increases with increasing specific surface (decreasing particle size). Since this Laboratory does not have facilities for measuring flour particle size, it was not possible to determine the exact relationship between the rate of bromate reaction and the specific surface area. It is anticipated that establishment of such a relationship would be complicated by a particle heterogeneity factor which might be different for different particle size fractions.

General Discussion

An attempt will first be made to explain the observed difference between the bromate reactions in continuously mixed and normal doughs in terms of the theory of rate processes (4). In normal doughs the initial reaction, which is analogous to the reaction in continuously mixed doughs, gives place to what appears to be a linear reaction. The most probable explanation is that some physical factor, not necessarily wholly inoperative during mixing, becomes rate-controlling in a resting normal dough. Both the initial reaction in a normal dough and the reaction in a continuously mixed dough are quantitatively described by equation 2 whereas the linear phase of the reaction in a normal dough is described by equation 3.

The large difference in the rates of the reaction in the doughs subjected to the two types of treatment cannot be explained on the basis of the small, almost insignificant difference in the activation energies. Nevertheless, the slightly lower activation energy for the reaction in the normal dough suggests that the activation energy of the physical process is probably somewhat lower than that of the chemical reaction.

On the other hand, the difference in the frequency factor is significant and parallels quite closely the difference in the amount of reaction in the two types of doughs. The frequency factor is directly related to the entropy of activation (4), and it therefore can be concluded that the physical rate-controlling factor affects this thermodynamic parameter. It is postulated that the increase in the entropy of activation as a result of continuous mixing occurs because reaction sites which may otherwise be sterically inaccessible are uncovered and increase the probability of effective collisions.

If the physical accessibility postulate is correct, then it might be possible to substantiate it experimentally by determining the rate of bromate disappearance in doughs prepared from flours of different particle size. Results of Fig. 4 showed that the rate increases as the particle size of the flour decreases. Since it is difficult to presume that reduction of a coarse farina to flour would produce new sulfhydryls by physically rupturing disulfide linkages, the increase in the bromate reaction must be due to an increase in the accessibility of the sulfhydryl groups with which the bromate ion seems to react. It should be emphasized that demonstration of the physical accessibility factor in the bromate reaction is possible only because the rate of the chemical reaction is of the same order of magnitude as the rate of the physical process. The evidence that the effect of con-

tinuous mixing is analogous to an increase in specific surface indicates that flour particles, mixed into a dough, retain a certain amount of the original identity, which probably decreases during prolonged mixing owing to a continuous shearing-off of the gluten layer formed on the external surface of the flour particle during dough development. The possibility that flour particles retain their identity in dough offers an interesting avenue of research on the physical properties of dough.

In conclusion, it should be pointed out that although the findings reported in this paper appear to cast some doubt on the usefulness of the results obtained with normal doughs for elucidating the mechanism of the bromate reaction, such results are necessary for our understanding of the reaction that occurs under a range of conditions used in baking technology. The effects of continuous mixing and flour particle size seem to complicate the kinetics slightly; however, it will be the understanding of all aspects of the bromate reaction in dough that will ultimately yield the mechanism of the improver reaction. The results of the continuous mixing experiments do indicate that the bromate reaction in doughs handled according to the more traditional baking practice is probably different from that in doughs produced by the high-speed mixing and mechanical development employed in modern baking technology. The results obtained with flours of different particle size indicate that special precautions must be observed in studying bromated doughs from flours prepared by the air-classification process.

Literature Cited

1. BUSHUK, W., and HLYNKA, I. The bromate reaction in dough. I. Kinetic studies. *Cereal Chem.* **37**: 141-150 (1960).
2. BUSHUK, W., and HLYNKA, I. The bromate reaction in dough. II. Inhibition and activation studies. *Cereal Chem.* **37**: 343-351 (1960).
3. CUNNINGHAM, D. K., and ANDERSON, J. A. Decomposition of bromate in fermenting and nonfermenting doughs. *Cereal Chem.* **33**: 290-299 (1956).
4. GLASSTONE, S., LAIDLER, K. J., and EYRING, H. *The theory of rate processes*. McGraw-Hill: New York (1941).
5. HLYNKA, I., and ANDERSON, J. A. Laboratory dough mixer with an air-tight bowl. *Cereal Chem.* **32**: 83-87 (1955).