

THE BROMATE REACTION IN DOUGH

I. Kinetic Studies¹

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ABSTRACT

The reaction of the bromate ion in nonfermenting doughs was studied under various conditions by determining residual bromate by the amperometric titration method. The over-all reaction is characterized by two distinct phases: a rapid initial reaction that occurs almost completely during mixing, and a slower, secondary reaction that proceeds at a constant rate. Reaction orders with respect to bromate concentration were found to be about 1.0 and 0.7 for the initial and the linear reactions respectively. Rates of both phases increase with increasing flour concentration and decreasing pH. The activation energies obtained for the range 10° to 50°C. are 1.48 and 10.16 kcal. per mole for the initial and linear reactions, respectively.

The effect of bromate on the physical properties of dough has attracted the attention of cereal chemists for a long time, and papers dealing with various aspects of the bromate reaction in dough have been published (3,6,8). However, no plausible mechanism for this reaction has so far been worked out.

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It has been demonstrated recently in this Laboratory that the amperometric titration can be used to determine residual bromate ion in dough (1). This procedure was also used successfully to follow the progressive disappearance of bromate in normal and modified doughs (1,2). It seemed desirable to continue the kinetic studies of the bromate reaction in dough, as they offer a reasonable approach to formulation of a mechanism for the reaction. Such information might be useful in explaining the action on the physical properties of dough of potassium bromate and similar agents.

This paper deals with the effects on the reaction rate in nonfermenting doughs of a number of factors normally investigated in kinetic studies, namely, bromate concentration, flour concentration, hydrogen ion concentration, ionic strength and temperature.

Materials and Methods

An untreated, straight-grade flour, milled commercially from hard red spring wheat, was used for all studies. Starch, used as a diluent in one experiment, was separated from the same flour. The flour was mixed into a dough and worked up by hand in a beaker of tapwater, and excess water was decanted after centrifuging. Resuspending in water and centrifuging for 15 minutes at 2,000 r.p.m. served to separate squeegee and granular starch. The latter was air-dried to a moisture of 12.7%. The flour and starch had protein contents of 13.2% and 0.21% and ash contents of 0.46% and 0.15% (14% moisture basis).

Some minor modifications were made in the methods (1) previously used for preparing and handling the doughs. Prior to mixing, the flour was evacuated and stored overnight under nitrogen in a vacuum desiccator. Air was removed from the liquids used by bubbling nitrogen through for 5 minutes. Doughs were mixed for 5 minutes in the GRL mixer (4) under nitrogen to 60% absorption, except where indicated otherwise. Gas analyses showed that the atmospheres under which the flour was stored and mixed contain small amounts of residual oxygen. The effect of this oxygen on the bromate reaction was neglected. During an experiment, the dough was stored at 30°C., except in the temperature study, at about 85% relative humidity. In the temperature study, the dough was mixed and stored at 10°, 20°, 40°, and 50°C., in addition to the normal temperature of 30°C.

Residual bromate was determined immediately after mixing and at hourly intervals up to 5 hours. The extraction procedure was essentially the same as outlined previously (1), except that the quantity of dough was reduced to 20 g. and extraction liquid comprised 90 ml. of water, 12.5 ml. of 1.04*N* zinc sulfate solution, and 12.5 ml. of 0.65*N*

sodium hydroxide solution. After dispersion in a Waring Blendor for 3 minutes at low speed and centrifugation, duplicate 20-ml. aliquots were titrated (1).

The potassium bromate concentration in mg. per kg. of dough (60% absorption) is obtained from the results for 20-ml. aliquots by multiplying the difference between the blank and sample titrations in ml. by 9.046.² The calculation of this factor involves measurement of the total volume of the dispersion containing 20 g. of dough and the 115 ml. of extraction liquid. For 60% absorption this volume is 130 ml.

Results and Discussion

Treatment of Results. In earlier papers (1,2), results were reported on a flour basis in p.p.m. of potassium bromate and were plotted in terms of residual bromate. For this study, it was found more convenient, and analogous to practices in solutions, to report results on a dough basis in mg. of potassium bromate per kg. and to plot them as bromate reacted. In the new terminology, 18.75 mg. of potassium bromate per kg. of dough of 60% absorption is equivalent to 30 p.p.m. of potassium bromate in a flour of 14% moisture content.

The calculations used in processing the data are illustrated in Table I and Fig. 1, which show results for a typical experiment with 18.75 mg. per kg. initial bromate in a dough of 60% absorption.

TABLE I
DATA FOR A TYPICAL EXPERIMENT AT 18.75 MG. PER KG. POTASSIUM BROMATE
AND 60% ABSORPTION

REACTION TIME	SAMPLE TITRATION	BLANK ^a - SAMPLE V	RESIDUAL BROMATE V × 9.046 = K	BROMATE REACTED 18.75 - K
hours	ml	ml	mg/kg	mg/kg
0	18.75	0
0.08 ^b	3.11	1.92	17.37	1.38
1	3.35	1.68	15.20	3.55
2	3.43	1.60	14.47	4.28
3	3.57	1.46	13.21	5.54
4	3.73	1.30	11.85	6.90
5	3.86	1.17	10.58	8.17

^a Blank titration = 5.03 ml.

^b First determination at approximately 3 minutes after mixing.

Figure 1 shows the amount of bromate reacted as a function of reaction time. It seems that the over-all reaction investigated consists of two relatively distinct phases, namely, a rapid initial reaction which occurs almost entirely during mixing, and a slower secondary reaction

² Potassium bromate, mg. per kg. of dough = (blank, ml. - sample, ml./1000) × (N of iodate) × V(ml.)/20 × 167.01/6 × 1000/20 × 1000 = (blank, ml. - sample, ml.) × 9.046 for N = 0.001 and V = 130 ml.

in which the disappearance of bromate varies approximately linearly with reaction time. In this paper, the reaction will be characterized by the amount of bromate reacted in the initial reaction and the rate of the linear reaction. The amount of bromate reacted was adopted as an index of the initial reaction, since it is not possible to measure the initial rate with any degree of accuracy. These parameters are determined as shown in Fig. 1.

Effect of Bromate Concentration. Table II summarizes the results of experiments at 30°C. and 60% absorption for different initial bromate concentrations. The concentrations of potassium bromate used are given in the first column in p.p.m. of flour and in the second in

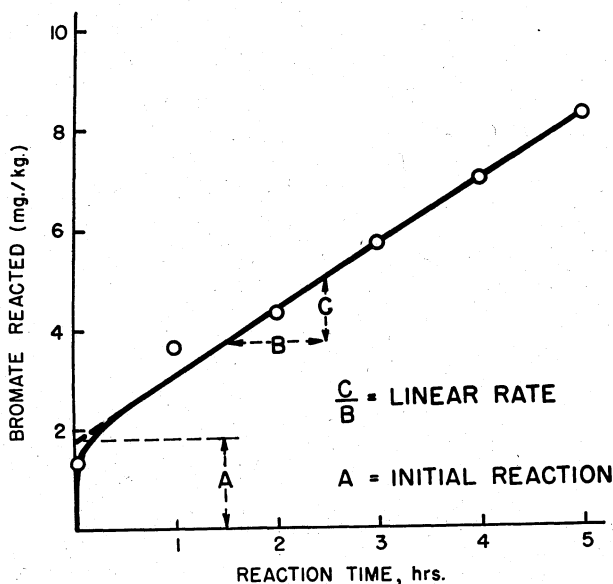


Fig. 1. Bromate reacted as a function of reaction time at 30°C. and 60% absorption, with initial potassium bromate concentration of 18.75 mg. per kg. of dough.

TABLE II
RESULTS WITH VARIOUS INITIAL POTASSIUM BROMATE CONCENTRATIONS
(Absorption = 60%)

BROMATE CONCENTRATION		INITIAL REACTION	LINEAR RATE
ppm flour	mg/kg of dough	mg/kg	mg/kg/hour
5	3.12	0.50	0.40
10	6.25	1.10	0.60
15	9.37	0.90	0.86
20	12.50	1.30	0.97
30	18.75	1.80	1.28
40	25.00	2.40	1.30

mg. per kg. of dough. The third and fourth columns give the amounts of initial reaction and the linear rates respectively.

The relation between the amount of initial reaction and the initial bromate concentration seems to be linear, whereas the rate of the linear reaction increases with increasing bromate concentration according to a relation that is definitely curvilinear (Fig. 2). A similar curvilinear relation results if the linear rate is plotted against initial bromate concentration corrected for the amount of initial reaction.

Determination of the reaction order with respect to bromate concentration, by plotting the logarithm of the rate against the logarithm of the concentration, gave an order of about 1.0 for the initial reaction and 0.7 for the linear reaction at low bromate concentrations. The order of 0.7 appears to decrease as the bromate concentration exceeds 18.75 mg. per kg. In making the logarithmic plot for the initial reaction it was assumed that the rate was directly proportional to the amount reacted.

Similar analysis of the data for the linear reaction for four flours published by Cunningham and Anderson (1) gave a reaction order of the same magnitude for three of the flours; the order for the fourth flour was about 0.4.

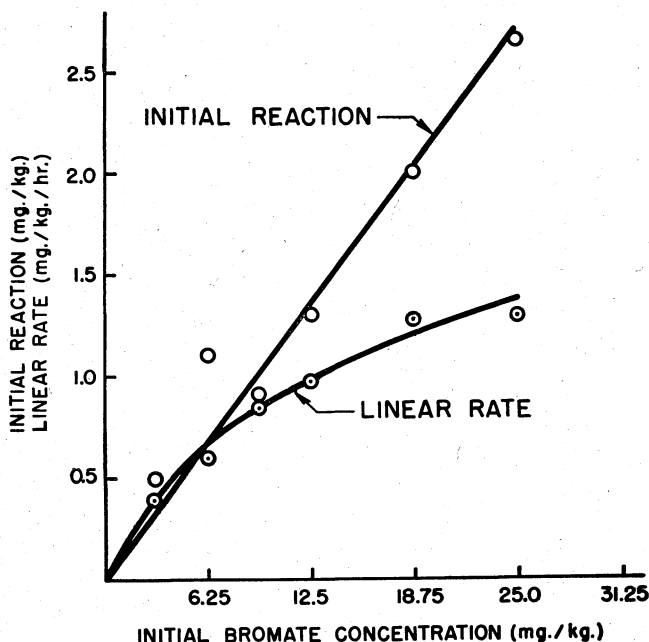


Fig. 2. Amount of initial reaction and rate of linear reaction at 30°C. and 60% absorption, as a function of initial potassium bromate concentration.

Effect of Flour Concentration. In an attempt to vary the concentration of the component of flour which reacts with the bromate ion, it was necessary to study the rate of bromate reaction in doughs containing different amounts of water (various absorptions). This created the problem of whether the bromate concentration should be kept constant on the basis of total dough weight or on the basis of the amount of liquid used to mix the dough. The former method was adopted because it seemed to be more in line with the method adopted initially for expressing bromate concentration.

The results that were obtained for the range of absorptions that could be used in the GRL mixer, with the initial bromate concentration of 18.75 mg. per kg., are plotted in Fig. 3. Although the total varia-

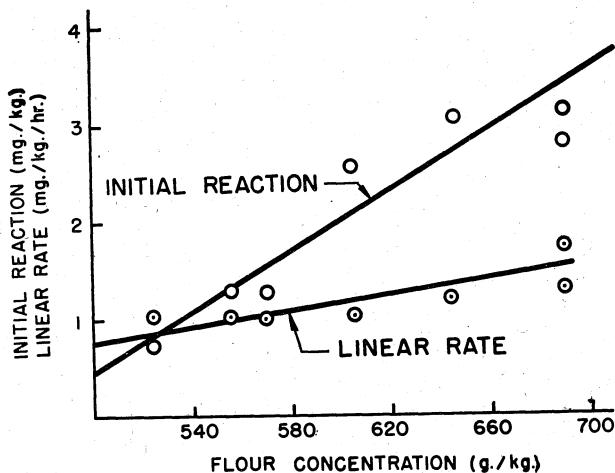


Fig. 3. Amount of initial reaction and rate of linear reaction at 30°C., as a function of flour concentration obtained by varying the absorption.

tion in flour concentration was only about 1.5 times, it seems that, in spite of the scatter, both the amount of initial reaction and the linear rate increase approximately linearly but at slightly different rates with flour concentration.

The effective concentration of the reactive component of the flour can also be varied by diluting the flour with the nonreactive component(s). In this manner the maintenance of a constant bromate concentration is simplified, since a constant absorption can be used. Experiments were therefore made with doughs from flour samples which were diluted by additions of starch.

Figure 4 shows the results of two levels of starch used with initial bromate concentration of 18.75 mg. per kg. and 60% absorption. It is

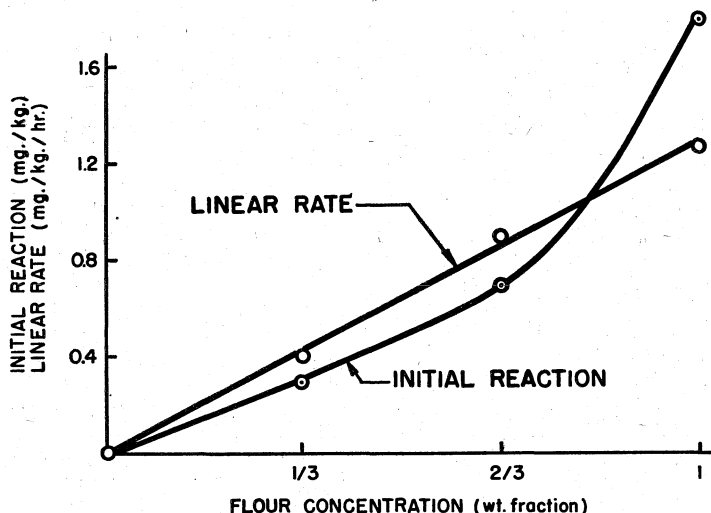


Fig. 4. Amount of initial reaction and rate of linear reaction at 30°C. and 60% absorption, as a function of flour concentration obtained by diluting the flour with starch.

apparent that both the amount of initial reaction and the linear rate increase with increasing flour concentration. These data indicate also that of the components of flour, it is not the starch that reacts with the bromate. Further studies of the bromate reaction in doughs mixed from various flour fractions may lead to a more specific localization of the reaction site or group.

Effect of Hydrogen-Ion Concentration and Ionic Strength. A study of the effect of pH on the bromate reaction in dough was made for two reasons. The first is that stoichiometric equations for oxidations by the bromate ion involve hydrogen ions, so that the pH dependence of the bromate reaction should give some indication of whether bromate reacts in dough as an oxidizing agent. The second reason is that a marked pH effect on the bromate reaction has been recently demonstrated by structural relaxation studies (5), and it was of interest to verify these observations by a different method. Studies on the effect of ionic strength can be useful in identifying certain types of ionic reactions.

Table III gives the results of experiments on doughs of pH varying from 4.2 to 8.7 as measured by the Beckman Zeromatic pH meter equipped with rugged electrodes. The pH of the dough was varied by adding predetermined quantities of hydrochloric acid or sodium hydroxide solution to the liquids used to mix the doughs. The actual amounts used are shown in Table III. The initial bromate concentra-

TABLE III
EFFECT OF pH ON THE BROMATE REACTION
(Initial potassium bromate = 18.75 mg./kg.; absorption = 60%)

pH	LIQUIDS, 90 ML. (+ 30 ml. of Bromate Solution)	INITIAL REACTION	LINEAR RATE
		mg/kg	mg/kg/hour
4.2	0.04N HCl	3.40	1.83
4.8	0.02N HCl	2.20	1.46
5.8	Distilled water	1.80	1.28
7.2	0.04N NaOH	1.80	1.10
8.7	0.08N NaOH	1.80	0.50

tion used was 18.75 mg. per kg. and the absorption was 60%. The reaction curves at pH values other than the normal pH of the dough (5.8) were of the same general shape as the normal curve.

Figure 5 shows the amount of initial reaction and the linear rate as a function of dough pH. The amount of initial reaction increases markedly with decreasing pH on the acid side but seems to be independent of pH on the alkaline side of the pH of a normal dough. The rate of the linear reaction varies inversely with pH over the range investigated. These findings are in general agreement with the hypothesis that bromate reacts as an oxidizing agent in dough and with the conclusions made by Hlynka and Chanin (5) based on the effect of pH on the rheological properties of dough.

Another possible explanation for the marked pH effect is the effect of hydrogen ions on the ionization of the reactive group of the flour. At present there is no evidence for or against this hypothesis.

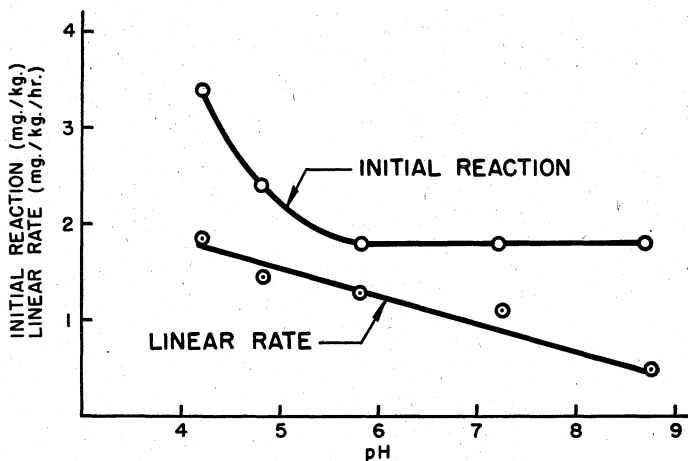


Fig. 5. Amount of initial reaction and rate of linear reaction at 30°C. and 60% absorption, as a function of dough pH.

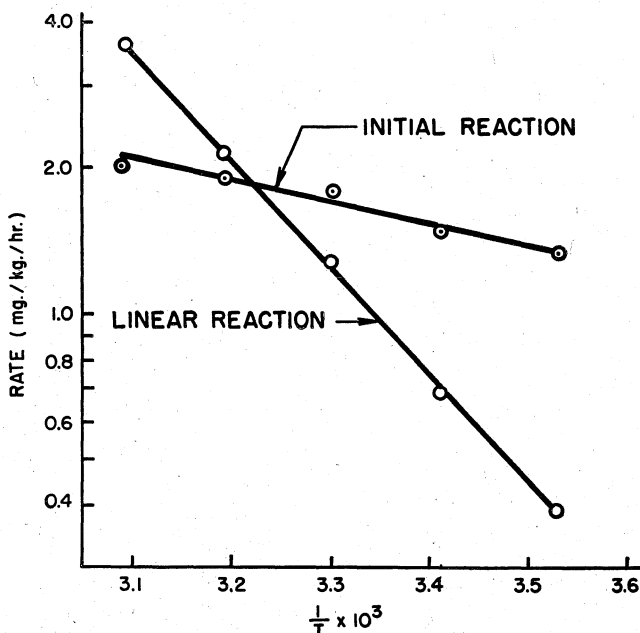


Fig. 6. Rates of initial and final reaction (logarithmic scale) at 60% absorption, as a function of the reciprocal of the absolute temperature.

The bromate reaction was not affected by variations of ionic strength by additions of up to 1.8% (flour basis) of sodium chloride. Accordingly, it appears that the bromate ion reacts with a neutral group rather than with another ion.

Effect of Temperature. Figure 6 shows the effect of temperature, plotted in the usual manner, on the two phases of the bromate reaction covering a temperature range of 10° to 50°C. Both the amounts of initial reaction and the linear rates plotted against $1/T$ give exceptionally good straight lines.

The activation energies obtained from the slopes of the lines in Fig. 6 are 1.48 kcal. per mole and 10.16 kcal. per mole for the initial and the secondary phases respectively. In the calculation of the activation energy for the initial reaction, it was assumed that the rate of the initial reaction is directly proportional to the amount of initial reaction, as was done in the analysis of the effect of bromate concentration.

General Discussion

The evidence presented in this paper suggests that the disappearance of bromate during the so-called initial reaction is real and not an experimental artifact as implied by Lee, Tkachuk, and Finlayson

(7). The two phases of the over-all bromate reaction are affected by the various factors examined in a similar way; accordingly, it is probable that the linear reaction may depend on the initial reaction. The activation energy of 1.48 kcal. per mole for the initial reaction suggests that the rate of this reaction is controlled by a physical process such as diffusion (mixing).

A reaction order of 0.7 with respect to bromate concentration for the linear reaction is not inconsistent with the fact that the over-all order appears to be zero. Such results are possible for extremely slow reactions. The activation energy of 10.16 kcal. per mole obtained for the linear reaction is in the range of values for reactions involving the breakage and formation of covalent bonds, although it does not rule out the possibility that activated diffusion might be the rate-controlling factor.

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