DECOMPOSITION OF POTASSIUM BROMATE IN WHEAT-FLOUR DOUGHS

by

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Being a thesis presented to the Faculty of Graduate Study
and Research in partial fulfilment of the
requirements for the degree of
Master of Science

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September 1952

ACKNOWLEDGEMENT

The author is indebted to Dr. I. Hlynka, Chemist at the Grain Research Laboratory, Board of Grain Commissioners, Winnipeg, who initiated the research and whose careful guidance throughout the course of the work was of great value. Grateful appreciation is extended to Dr. J. A. Anderson, Chief Chemist of the Grain Research Laboratory, for his continued interest in the project and for making available the facilities of the laboratory where the research was carried out.

Acknowledgement is made to Dr. A. D. Robinson, Professor of Biochemistry, the University of Manitoba, for his interest in the work and for his help in preparation of the thesis.

A grant from the National Research Council financed the research.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

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INTRODUCTION

Wheat flour does not exhibit its maximum baking potentialities if it is used immediately after milling. However, if the flour be stored for a period of several months, or if certain chemical reagents be added to the fresh flour, the optimum baking qualities will manifest themselves. This phenomenon is known to the baking trade as "improvement" and the chemical reagents are termed "improvers". Since the storage method of flour improvement is time consuming and demands greater storage facilities and extra handling of the flour, it has given way to the more expedient chemical method.

From the time it was first discovered that chemical agents could preclude the need for a storage (or natural aging) period for flour, numerous compounds have been tried as flour improvers. From the number (which included such substances as ammonium persulfate, nitrogen trichloride, potassium bromate, and ascorbic acid) potassium bromate has risen to highest popularity. This is because it is convenient to handle, is required in only very minute amounts (around 10 p.p.m. of flour) to produce a maximum amount of improvement and it has no secondary objectionable qualities that deter the consumption of bread that has been baked with it.

Since potassium bromate is widely used as an improver it is desirable to know as much as possible about its physico-chemical reactions in the dough. The outward physical changes in dough and bread that are effected by added bromate are obvious to the trained eye: e.g., a more elastic dough, greater loaf volume, finer crumb texture, silkier appearing crumb. However the exact chemical nature of the reaction of bromate, that causes these changes, is not clear. This has been the subject of much investigation and speculation in the literature.

At present the literature reveals that the generally accepted hypothesis is that bromate acts as an oxidizing agent in its role of improver. Decomposition or reduction of bromate in bread dough has been reported as evidence for this hypothesis. If oxidation-reduction is, in fact, the mechanism of improver action then a more detailed study of the reaction is required. On the other hand, if the decomposition of bromate is not concerned with the improving action, but is merely a concurrent reaction, this aspect, too, merits study. In either case the study undertaken here will give greater insight into the mechanism of improver action by inquiring into the various issues that arise out of the hypotheses.

Some of the fundamental and important aspects of such a study are the effects of time, temperature and concentration. Bromate decomposition with time at a constant temperature and different concentrations of reactants is studied here. The effect of mechanical action, such as mixing or working in the extensograph machines is also investigated. One other important facet of such a study is the influence of pH on the reaction. This too has been approached. There is also a report given on the work done at the Grain Research Laboratory in Winnipeg, which prefaced this thesis.

However, there is more to be gained by such studies. Bread constitutes a major portion of the world's diet and as such should be under continual study with regard to improving it as a nutriment source. Any scientific investigation that is concerned with the constituents of bread and their interaction will add to the stockpile of knowledge. It is superfluous to say that the more we know about a food substance the better use we can make of it and the more we can do to improve it. It is felt that the work presented here constitutes a positive contribution to the knowledge of the improvement of wheat-flour dough by potassium bromate.

LITERATURE REVIEW

There is little reported in the literature directly concerning the mechanism of the decomposition of bromate in dough but numerous investigations dealing with the nature of the improving action of potassium bromate in wheat-flour doughs as it is related to the oxidizing action of bromate, are to be found. This review outlines the work and opinions of those investigators who seek an answer to the enigma of the improvement of bread dough by bromate.

One of the first hypotheses on the nature of the improving action of bromate was the one concerning oxidation. Early mention of this was made by Geddes (14). He reasoned that bromate oxidized, and thereby inactivated, certain wheat germ constituents, presumably the phosphatides, which had a deleterious effect on the dough. More recently, Sullivan, Howe, Schmalz and Astleford (35) agree that the germ has harmful effects on the flour but attribute it to its glutathione content. However, they say that all flours which responded to bromate did show the amount of reducing substances to be expected.

Saunderson (32) conducted a series of comparative baking tests on flour germ mixtures using $NaBrO_3$, $KBrO_3$, KIO_3, CaO_2 and $K_2S_2O_8$. These were added in amounts which were calculated to yield the same quantities of oxygen. The effect of the several improvers was not proportional to their oxidizing power, but seemed to be a specific effect of the salt used.

Ziegler (39, 40) says that bromate acts gradually as an improver due to its slow rate of oxidation of glutathione. He also found that small amounts (1 in 25,000) of oxidized glutathione had a beneficial effect on dough and so improvement caused by bromate is not merely due to suppression of the harmful effect of the protease activator reduced glutathione. He also notes that at temperatures below 40°C. an enormous overdose of bromate is necessary for the rapid oxidation of glutathione. Further studies by Ziegler (41) on the oxidation of glutathione by various chemicals and the improver action of these revealed that only bromate showed the improver effect.

Another approach to the question of the nature of the improver action of potassium bromate concerns proteolysis. Jorgensen (24) as well as Balls and Hale (5) believe the flour contains "powerful but latent" proteolytic enzymes of the papain type which are activated by SH compounds and inactivated by bromate. The extremely small amount of oxidant required, said Balls and Hale, is not surprising because its action is not on the main constituents of the system but on a catalyst, itself present only in traces. Jorgensen suggests that over improvement results when the bromate depresses the proteolysis in the dough below a certain optimum amount. Jorgensen supports his theory by pointing out the depression in the amount of soluble nitrogen caused by bromate in a dough treated with papain.

Shen and Geddes (33) found that bromate considerably depressed proteolytic activity as indicated by the lower amino nitrogen levels at corresponding fermentation times. They also found that the bromate requirements to produce a satisfactory dough increased as the flour contained more reducing matter and protease.

However, Swanson (37, 38) found from a study of mixogram curves that those obtained from autolyzed doughs were similar to those obtained with use of papain but, if this change were due to enzyme action, it was only slightly influenced by the presence of $KBrO_3$. Even when using bromate in amounts as high as 72 mg. for doughs made with 35 g. of flour, it could not be shown from the characteristics of the recording mixer curves that the bromate had any inhibiting effect on proteolysis.

Sullivan, Howe, Schmalz and Astleford (35) point out that not all chemists are agreed that the effect of improvers such as bromate is to be attributed to their effect in inhibiting the proteolytic enzymes. They believe that glutathione and other SH compounds acted mainly per se on the gluten and not indirectly as an enzyme activator. They review their work on the influence of oxidizing agents on the lipids, gassing power, diastatic activity, starch, sugars, fermentation and gluten. They conclude that changes in the sulfur linkages of the gluten proteins are responsible for many of the effects described as improvement. Baker, Parker and Mize (4) also indicated that the reaction of oxidizing agents on dough is located either in the gluten or in the water-soluble portion of the dough. Sullivan (36) elaborates on this by stating that some if not all of the disulfide groups of the proteins of flour form cross linkages between polypeptide chains. These cross linkages exert a profound influence on the physical properties of gluten. Reducing agents affect the dough structure by virtue of destroying such linkages; oxidizing agents, by helping to form new linkages.

This question of the mechanism of bromate action in dough has been approached from other angles. Among these are the effect of bromate on carbon dioxide production, on carbon dioxide retention, on the colloidal properties of the dough, and as an oxidizing agent in the dough.

With regard to the effect of bromate on carbon dioxide production and retention Harris (16) noticed changes in loaf volume when diastatic malt was included in the baking formula along with bromate. Geddes and Larmour (15), Larmour and Brockington (27) and Saunderson (32) found that bromate does not influence the rate nor the amount of CO_2 production in bread doughs but modifies their gas retaining capacity. Studies on wheat germ by these workers indicate that the action of bromate on gluten quality is largely indirect. But they also found that oxidation is not the only or indeed the principal effect of chemical improvers in bread doughs.

Freilich and Frey (12) deal with the aspect of oxidation and mixing effects. They found that even when mixing in excess of oxygen with the dough no excess-bromate effect was observed. There seems to be a fundamental difference between the effects of oxygen and bromate on dough. They also found that bromate and prolonged fermentation tend towards "over improvement", but remixing of the dough eradicates this effect. They say (10) that this suggests that the improvements may be due mainly to a physical change in the colloidal properties of the dough. Saunderson (32) makes a similar suggestion saying that the effect of potassium bromate is directly on the colloidal nature of the gluten proteins and the effect which it has on loaves baked with phosphatides present is concurrent with the effect of those substances rather than directly on them.

In recent work by Holme and Spencer (18) the effect of bromate on sulfhydryl groups from different flour fractions was measured by means of a titration using iodosobenzoate which is specific for sulfhydryl groups. Bromate caused no apparent reduction in the sulfhydryl content of both gluten washings and flour slurries when held at room temperature. Added glutathione however was partially oxidized.

The addition of $KBrO_3$ to a flour slurry showed no decrease in the apparent sulfhydryl content at the end of 21 hours at room temperature. With these results in mind it would appear that flour improvers added to yeasted doughs must be used up in reaction with some other groups than the sulfhydryl groups which occur in the flour protein as determined with iodosobenzoate, during the stages of dough make up and fermentation.