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SOME IMPROVING EFFECTS OF HALOGENATES AND THEIR REDUCTION INTERMEDIATES IN DOUGH[1]

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ABSTRACT

As the reduction of bromate in dough probably involves the intermediates bromite, hypobromite, and bromine, a comparison of the effect of hypobromite, bromine, chlorite, hypochlorite, and chlorine with bromate and iodate was carried out by extensigraph and baking studies on wheat doughs. The results indicate that the relatively slow reaction of bromate is due to the first reduction stage of bromate to bromite, and the first and second reduction stages (bromate → bromite →) cause the most efficient chemical reaction of the functional groups directly responsible for the improving effect in dough. Sodium chlorite compares favorably with bromate and iodate as a flour improver. The remaining reagents act as less efficient improvers.

In acidic aqueous solutions containing bromide, bromate is converted to bromine, and the following sequence of reactions has been postulated by Hinshelwood (11):

$$HBr + HBrO_3 \rightarrow HBrO_2 + HOBr \quad \text{(Rate-controlling)}$$
$$HBr + HBrO_2 \rightarrow 2\ HOBr \quad \text{(Rapid)}$$
$$HBr + HOBr \rightarrow Br_2 + H_2O \quad \text{(Rapid)}$$

Bromine in the presence of suitable substances such as oxalate, is reduced to bromide (11):

$$Br_2 \rightarrow Br^- + Br^+$$
$$C_2O_4^= + Br^+ \rightarrow 2\ CO_2 + Br^-$$

This hypothesis is, in general, consistent with the results obtained from other studies of the reduction of bromate (1,2,10).

It would seem reasonable then, to assume that the reduction of bromate (3,13) or iodate (5) in dough proceeds in a similar manner and involves intermediate reduction entities such as bromite, hypobromite, and bromine. Thus the improver effect of bromate may be partly due

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to one of these intermediates or to a combination of all or most of them. Some aspects of this matter are examined in the present paper.

As it is difficult to prepare bromite free from mercuric salts (4), experiments were restricted to studies of hypobromite and bromine; but the corresponding chlorine homologues (10), chlorite, hypochlorite, and chlorine, were included together with the well-known improvers bromate and iodate. The effects of these reagents were tested by means of both extensigraph and baking methods. Gassing power was checked in order to ensure that baking performance was not affected by possible inhibition of the yeast.

Materials and Methods

Hypobromous acid was prepared by the addition of excess silver orthophosphate to an aqueous bromine solution. After the bulk of the insoluble material was removed by centrifuging, vacuum distillation yielded pure hyprobromous acid (1). Hypochlorous acid was prepared in a similar manner.

Hypobromous acid and bromine solution were freshly prepared every day; sodium chlorite, hypochlorous acid, and chlorine solutions every second day; and all were stored in amber-colored bottles at 4°C., with minimum exposure to light. All solutions were analyzed for their oxidizing power towards acidic potassium iodide solutions by amperometric titrations (6).

The flour was a commercial, straight-grade, unbleached and nonimproved sample (13.5% protein) from a blend of Canadian hard red spring wheat. Doughs for extensigraph studies were mixed under an atmosphere of nitrogen, and relaxation constants were determined as previously described (7,8). Baking tests were made by the basic AACC method with 2% yeast and an absorption of 59%; and gassing powers were determined by the AACC pressuremeter method (12).

Results and Discussions

The extensigraph data are given in Fig. 1 as a plot of the relaxation constant against the reaction time. Curves for the bromine and chlorine compounds tested are shown in the upper and lower portions respectively, as solid lines; for purposes of comparison, curves for bromate and iodate, and control doughs, are included as dotted lines.

Figure 1 shows that hypobromite is a more effective improver than bromine, but that neither is as effective as bromate. Moreover, whereas bromate reacts slowly, hypobromite and bromine react quite quickly in dough. This was confirmed by amperometric titrations of dough extracts, which showed that these two reagents were not present 4

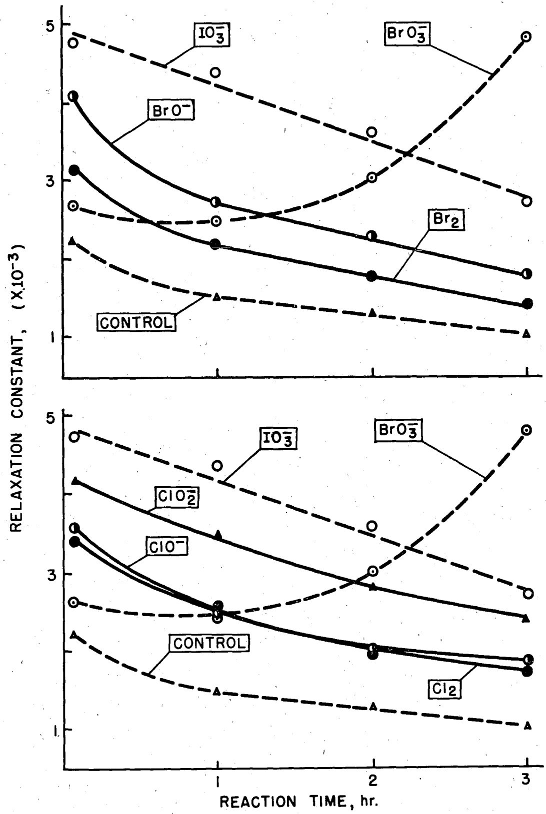

Fig. 1. Relation between the relaxation constant and reaction time. The dosages for Br_2, BrO^-, BrO_3^-, Cl_2, ClO^-, ClO_2^-, and IO_3^- are 125, 125, 75, 125, 125, 30, and 30 μeq. per 100 g. flour.

to 5 minutes after their incorporation into dough.

The lower portion of Fig. 1 shows the curves for doughs treated with chlorite, hypochlorite, and chlorine. All three act as improvers, and react rapidly as was confirmed by amperometric titration. Sodium chlorite is more effective than any of the other derivatives, but less effective than iodate or bromate; its effect on extensigraph properties of dough at a reaction time of 10 minutes has been noted previously (14). Hypochlorite and chlorine behave similarly, and are about intermediate in effectiveness between hypobromite and bromine.

It would have been ideal to have a direct comparison of all the reagents tested at a dosage corresponding to an equivalent oxidizing power. However, this is difficult to accomplish, because the range of the instrument is limited in that it cannot directly measure the large variation in dough properties caused by these reagents. Nevertheless, a very useful order of effectiveness of the reagents can be obtained by comparing the relaxation constants in Table I representing the dosages actually used. To obviate the difficulty of different dosages, calculated constants are also listed; these represent equivalent dosages of 30 μeq. per 100 g. flour for all reagents (i.e. for bromate, $4.8 \times 10^{-3} \times 30/75$).

TABLE I
RELAXATION CONSTANTS FOR NONFERMENTING DOUGHS CONTAINING VARIOUS HALOGEN COMPOUNDS

REAGENT	DOSAGE [a]	RELAXATION CONSTANT $\times 10^{-3}$	CALCULATED RELAXATION CONSTANT [b] $\times 10^{-3}$
BrO_3^-	75	4.8	1.9
IO_3^-	30	2.8	2.8
ClO_2^-	30	2.3	2.3
BrO^-	125	1.8	0.43
ClO^-	125	1.8	0.43
Cl_2	125	1.7	0.41
Br_2	125	1.4	0.34
Control	...	1.0	...

[a] Microeq. per 100 g. flour.
[b] Calculated to a dosage corresponding to 30 μeq. per 100 g. flour.

These data show that bromate, iodate, and chlorite are of the same order of effectiveness for increasing the resistance of dough to stretching, and that the remaining compounds tested are only about one-fifth as effective.

Baking tests were also made with the compounds. It was noticed that, with some reagents, the effect on loaf volume depended on the manner of addition and incorporation into the dough. For example, when hypobromite and yeast solutions were added separately to the flour just prior to mixing, only very slight loaf volume increases were obtained, even at dosages up to 344 μeq. per 100 g. flour. However, if the hypobromite and yeast solutions are added separately and simultaneously to a flour being continuously mixed, then reproducible loaf volumes resulted. The second procedure was therefore used in all the baking tests reported in this paper. Studies with each reagent also showed that, with this procedure, none had any effect on gassing power at dosages producing optimum loaf volumes — or at twice these dosages.

Loaf volumes obtained at various concentrations of each reagent are given in Fig. 2. Because one has to consider both the optimum loaf volume obtained and the dosage of the reagent used at this optimum (Table II), it is more difficult to list a definite order of efficiency. Nevertheless, it is obvious that there is a clear distinction between the behavior of bromate, iodate, and chlorite and of hypochlorite, chlorine,

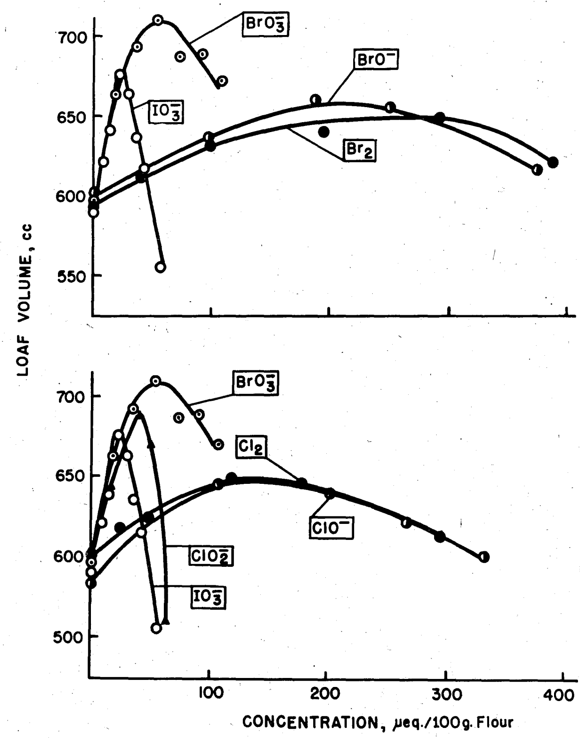

Fig. 2. Relation of loaf volume changes to added increments of various halogen compounds.

hypobromite, and bromine; the former group are at least twice as efficient as improvers. Thus we see that all the compounds tested increase the loaf volumes of baked bread, and in general these results are similar to and complement the results obtained from the rheological experiments. It is of interest to note here that chlorite produced

TABLE II
DOSAGES OF HALOGEN COMPOUNDS AT OPTIMUM LOAF VOLUMES

REAGENT	OPTIMUM LOAF VOLUME	DOSAGE AT OPTIMUM LOAF VOLUME	RELATIVE DOSAGE AT OPTIMUM LOAF VOLUME (21 µEQ. ≡ 1)
	cc	*µeq*	
IO_3^-	665	21	1
ClO_2^-	665	38	1.8
BrO_3^-	705	54	2.6
ClO^-	650	114	5.4
Cl_2	650	135	6.4
BrO^-	665	186	8.8
Br_2	640	200	9.5
Control	595	...	...

an optimum loaf volume slightly higher than that produced by iodate.

The first reaction in Hinshelwood's proposed series (11), given earlier, has been experimentally substantiated (1,2,10). Moreover, the present findings that bromine, hypobromite, and also bromite (by analogy to chlorite) react very quickly in dough further indicate that the reduction of bromate to bromite controls the rate of disappearance of bromate in dough also. All other reactions, including those of the chlorine homologues and probably the iodine homologues, appear to be rapid. It may be that the more highly oxidized compounds react with sulfhydryl groups, and that the remaining compounds are indiscriminate oxidizing reagents. Since it has been shown that small amounts of cysteinesulfenic and cysteinesulfonic acids are produced from cysteine by bromate (9), some indiscriminate oxidation of a similar type may be expected in dough. Though the principal reactions of bromate and other improvers in dough might yet prove to be relatively simple, the detailed stoichiometry is doubtless complex.

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