# A NOTE ON THE DISAPPEARANCE OF RADICALS TRAPPED IN GAMMA-IRRADIATED STARCH AND GLUTEN[1]

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Recently, Lee and Bhardwaj (1) reported the measurement of radical concentrations in gamma-irradiated flour by means of electron paramagnetic resonance (EPR) absorption. The disappearance of the surviving radicals trapped in the flour after irradiation was found to follow second-order kinetics, with the rates proportional to the second power of the concentrations of radicals. The present Note reports a similar study on wheat starch and vital gluten.[2]

TABLE I
CONCENTRATIONS OF RADICALS IN IRRADIATED STARCH AND GLUTEN

| TIME AFTER IRRADIATION | (SPINS/ML.) $\times 10^{-17}$ | | | |
|---|---|---|---|---|
| | STARCH | | GLUTEN | |
| | Dried | 5.7% Moisture | Dried | 6.5% Moisture |
| *days* | | | | |
| 0 | 11.27 | 9.08 | 3.05 | 1.14 |
| 1 | 10.26 | 4.45 | 1.22 | 0.28 |
| 2 | 9.15 | 2.77 | 1.07 | 0.21 |
| 3 | 8.23 | 1.83 | 0.95 | 0.20 |
| 4 | 7.94 | 1.22 | 0.71 | 0.15 |
| 5 | 7.88 | . . . | 0.62 | 0.12 |
| 6 | 6.68 | 0.37 | 0.57 | 0.11 |
| 8 | 6.20 | 0.28 | 0.56 | . . . |
| 10 | 5.07 | 0.0 | 0.53 | 0.092 |
| 12 | . . . | | . . . | 0.097 |
| 13 | 5.88 | | 0.49 | . . . |
| 15 | 5.14 | | 0.42 | 0.087 |
| 17 | 3.85 | | 0.50 | 0.097 |
| 20 | 3.08 | | 0.47 | 0.076 |
| 25 | 2.85 | | 0.58 | . . . |
| 29 | 2.49 | | 0.52 | . . . |
| 33 | 2.61 | | 0.38 | . . . |
| 37 | 2.27 | | 0.42 | . . . |
| 41 | 1.99 | | . . . | . . . |
| 49 | 1.44 | | 0.39 | 0.090 |
| 62 | . . . | | 0.50 | 0.071 |
| 75 | 0.89 | | 0.51 | . . . |
| 88 | 0.61 | | 0.42 | . . . |
| 102 | 0.25 | | 0.45 | 0.077 |
| 118 | 0.17 | | | |
| 137 | 0.0 | | | |

Dried starch and dried gluten (vacuum oven at 60°C. for 72 hr.), starch at 5.7% moisture (vacuum-dried at room temperature for 8 hr.),

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[2]The wheat starch and vital gluten were kindly supplied by the Research Department, The Ogilvie Flour Mills Co. Ltd., Montreal.

and gluten at 6.5% moisture (as received) were each subjected to irradiation with $10^6$ rads of $^{60}Co$ gamma-rays (2). The shape of the EPR spectrum of the irradiated wheat starch was very similar to that of corn starch reported by O'Meara and Shaw (3); the integrated absorption curve suggested an overlapping doublet. The EPR absorption of the irradiated vital gluten showed much lower intensity, and the integrated spectrum was a less resolved broad singlet. Not surprisingly, the spectrum of irradiated flour (1,2) showed more resemblance to that of starch than that of gluten.

Radical concentrations at various times after irradiation were determined according to the method previously described (1). The results are summarized in Table I. For kinetic behaviors of second order with respect to radical concentration, a plot of the reciprocals of concentration at time t, 1/(a—x), *vs.* t would give a straight line whose slope is the specific rate constant $k_2$. In the previous work with irradiated flour (1), the disappearance of radicals was followed up to 55 days and straight-line plots were observed in all cases. In the present studies with starch and gluten, disappearance of radicals was followed for longer periods, and the plots of 1/(a—x) *vs.* t are shown in Figs. 1 and 2. It can be seen that deviations from linearity occur in the latter stages of radical decay. From the linear part of these graphs, the slopes are

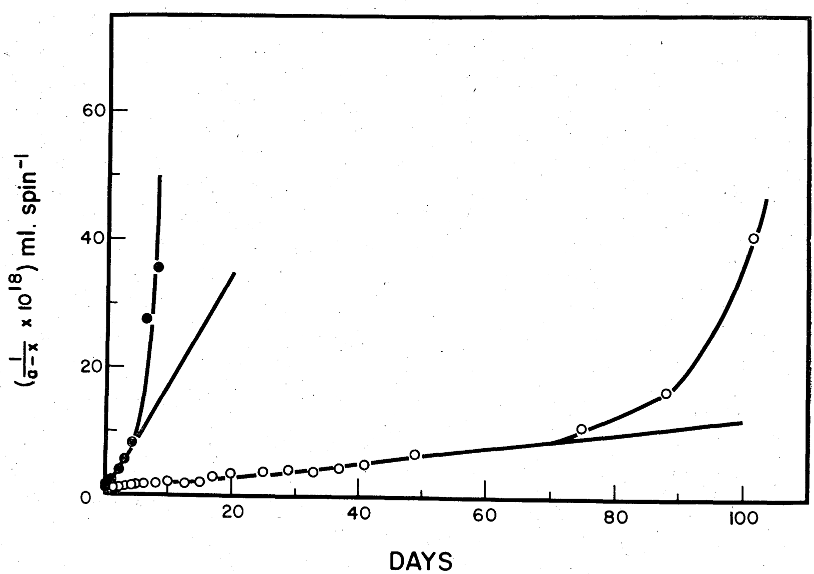


Fig. 1. Kinetic plots of reciprocals of radical concentration *vs.* time for wheat starch after irradiation with $10^6$ rads. Open circles, dried starch; closed circles, starch with 5.7% moisture.

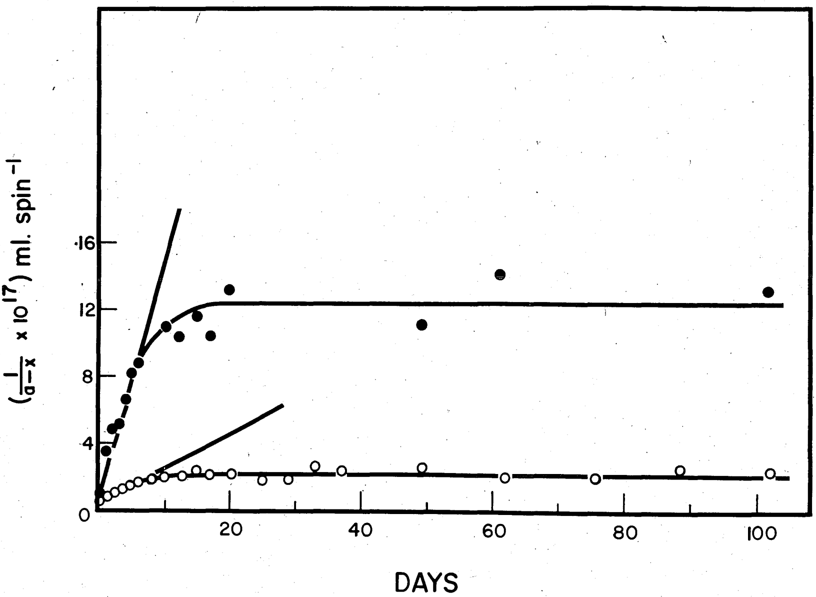


Fig. 2. Kinetic plots of reciprocals of radical concentration *vs.* time for vital gluten after irradiation with $10^6$ rads. Open circles, dried gluten; closed circles, gluten with 6.5% moisture.

$0.11 \times 10^{-18}$, $1.7 \times 10^{-18}$, $2.2 \times 10^{-18}$, and $12 \times 10^{-18}$ ml. spin$^{-1}$ days$^{-1}$, which are equivalent to initial second-order specific rate constants of $0.77 \times 10^{-3}$, $12 \times 10^{-3}$, $15 \times 10^{-3}$, and $84 \times 10^{-3}$ l. mole$^{-1}$ sec.$^{-1}$ for the dried starch, moist starch, dried gluten, and moist gluten, respectively. In the latter stages, the disappearance of radicals in starch was greatly accelerated; whereas in the gluten, a residual small concentration of radicals remained essentially constant for a long period of time.

The above results can be explained on the basis of the mechanism suggested by Lee and Bhardwaj (1) in that the second-order disappearance of the trapped radicals after irradiation likely is not due to recombination (equation 1), but may be attributable to reactions with species capable of destroying radicals such as water or the hydroxyl groups of carbohydrates (equations 2 and 3).

$$R\cdot + R\cdot \rightarrow R-R \quad (1)$$

$$R\cdot + HA \rightarrow RH + A\cdot \quad (2)$$

$$R\cdot + A\cdot \rightarrow RA \quad (3)$$

In the case of irradiated starch, when radical concentrations have decreased to a low level, an excess of hydroxyl groups would be present in comparison to the radicals, and hence in the latter stages of radical decay their destruction is greatly accelerated. In the irradiated gluten, the initial concentrations of trapped radicals are lower than in irradiated starch. These relatively low concentrations of radicals first undergo quite rapid reactions with accessible groups capable of causing destruction of radicals. However, after the initial reactions, the environment of the irradiated gluten must be such that a residual small amount of radicals remained relatively stable because, unlike starch, there is no great preponderance of hydrogen-donating groups in gluten to cause total destruction of the radicals, some of which may be produced in the inaccessible interior parts of the protein molecules.

## Acknowledgment

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