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Radiation Chemical Studies of Protein Reactions: Effect of Post-irradiation on the Breaking of Secondary Bonding in Protein

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SUMMARY

When protein was irradiated by γ -rays from a ^{60}Co source, a post-irradiation effect of the breaking of secondary bonding in protein was caused. An empirical equation for the reactivity decay was obtained, and the phenomena were explained on the basis of molecular mechanism.

INTRODUCTION

It is well known that reactivity of irradiated molecules varies with the time after irradiation [1-7]. Since the effect of radiation in protein is a problem of general interest [8-10], it was decided to investigate the effect of post-irradiation on the breaking of secondary bonding in protein.

The breaking of hydrogen bonds in gelatin molecules caused by urea was selected to study the breaking of secondary bonding in protein [10-12]. The determination can be conveniently followed by measuring the reduced viscosity of the solution as a function of the time after γ radiation [6, 8, 10].

EXPERIMENTAL

Materials

Gelatin used in this work was a commercial material produced by the Kanto Chemical Co., Inc. The urea used was a commercial material produced by the Junsei Pure Chemical Co., Ltd.

Apparatus and Procedure

An irradiation source containing about 1500 C of ^{60}Co was used. The dose rate in this work was 1.2×10^4 R/hr. The solid gelatin was irradiated in air at room temperature. At different times after irradiation the irradiated gelatin was dissolved with the urea solution. Then the viscosity was measured at 30°C [6, 8, 10].

RESULTS

Changes in the reduced viscosity of gelatin at different times after γ irradiation were studied in 5% gelatin in 8 M urea, 10^3 R, and 30°C . The results are shown in Fig. 1. From this it is clear that the decrease in the reduced final viscosity with a lapse of time after irradiation on the logarithmic scale indicates a post-irradiation effect on the breaking of secondary bonding in protein.

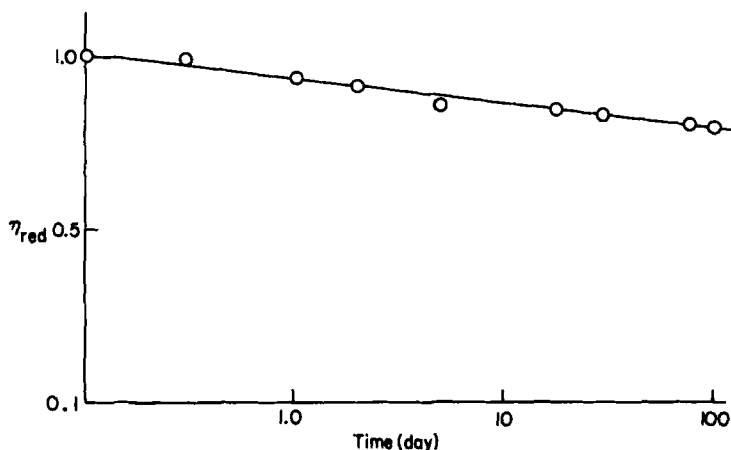
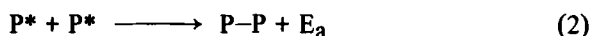


Fig. 1. Reduced viscosity vs. time after irradiation.

DISCUSSION

As stated above, it is known that the reactivity of an irradiated molecule varies with the time after irradiation [1-7]. The change in the breaking of hydrogen bonds was estimated from the change in reduced viscosity, and this change is given in Fig. 1. The relation between the change in reduced viscosity and the time after irradiation is related to that between the breaking of hydrogen bonds in the gelatin molecule and the time after irradiation. When the concentration of gelatin and urea and the radiation dose are all constant, a change with time after irradiation results in the change in reduced viscosity required for the breaking of hydrogen bonds in gelatin molecule; see Fig. 1. The reaction mechanism must, therefore, depend on the time after irradiation. If the main processes for the reactivity of gelatin are assumed to be



where $P-P$ is the gelatin molecule, P^* is the irradiated gelatin molecule, and E_a is the activation energy of γ -rays. The reactivity decay step may be Eq. (2), which means that the observed viscosity change is related to the time after irradiation. The response of the breaking of hydrogen bonds in gelatin molecule to the time after irradiation can therefore be determined by measuring the reduced viscosity.

The phenomena can be treated by applying a molecular mechanism described in the previous paper [7]. In any given unit volume of the irradiated gelatin there is a decay mechanism in which the relaxation process of reactivity can occur, and over which the reactivity distributes itself. In this unit process of decay the effect of reactivity on the rate of radiation is twofold. First, there is an activation component for which the rate of radiation in the hydrogen bonds in the irradiated gelatin molecule is related to the rate of reactivity, and second, there is a contribution to the rate of radiation of relaxation processes such as energy transfer or energy loss. It is convenient to classify the various unit process of decay into categories which group similar processes together. Suppose that there are N such parallel processes of reactivity hydrogen bond in a cubic centimeter of unit volume, so that if the total reactivity f distributes itself on this type of unit process of decay the average reactivity will be f/N . Suppose, too, that in the per unit distance of decay there are n such processes of decay in series. Then the total rate of radiation is given by

$$\frac{dr}{dt} = \frac{1}{R} \frac{df}{dt} + n\lambda \frac{kT}{h} \exp\left(\frac{-\Delta F^*}{kT}\right) 2 \sinh \frac{f}{2NkT} \quad (3)$$

where λ is the average distance projected in the reactivity space between equilibrium states in the relaxation process, and ΔF^* is the free energy of activation for the decay process. R is the appropriate partial constant to be associated with the decay process, and the first term on the right represents the activation contribution. The contribution to rate of radiation due to relaxation (energy transfer or energy loss) is given in the second term, and this term is derived by applying the theory of absolute reaction rates. The average reactivity f/N acts on the unit hydrogen bond and tends to favor motion from one equilibrium state to another in the reactivity space. The sum of all the partial reactivities on the decay mechanism is equal to the total reactivity, and the reactivity is distributed in such a way that the rate of radiation is the same for each.

Equation (3) can be written in a more condensed form

$$\frac{dr}{dt} = \frac{1}{R} \frac{df}{dt} + A \sinh Bf \quad (4)$$

Integration of Eq. (4) for the condition of constant radiation, $dr/dt = 0$, gives the following for the relaxation of reactivity

$$\tanh\left(\frac{Bf}{2}\right) = \tanh\frac{Bf_0}{2} \exp(-ABRt) \quad (5)$$

where f_0 is the initial reactivity. If $Bf/2$ is larger than unity and $f_0 > f > 1/2B$, then the approximate result is

$$f = \frac{1}{B} \ln\left(\frac{ABR}{2}\right) - \frac{1}{B} \ln t \quad (6)$$

Equation (6) can be written in a more condensed form

$$f = a - b \log t \quad (7)$$

Now, if the decay rate of the reactivity is proportional to the rate of reduced viscosity, then

$$\eta_{\text{red}} = a - b \log t \quad (8)$$

This formula agrees with the experimental data described in Fig. 1. This reduced viscosity behavior shows a dependence on reactivity decay similar to that of earlier experiments [6, 7].

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