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Radiation Chemical Studies of Protein Reactions: Effect of Irradiation Atmosphere on Viscosity

MIZUHO NISIZAWA, *Department of Chemistry, Defense Academy, Yokosuka, Japan*

Synopsis

When protein is irradiated by γ-rays from a ^{60}Co source in various atmospheres such as N_2, CO_2, H_2, O_2, and NH_3, the effect of the radiation varies with the gases composing the irradiation atmosphere. An empirical equation for the viscosity change was obtained.

INTRODUCTION

It is well known that some gases such as Xe, Kr, CO, and H_2O accelerate the radiation effect in polymers, while other gases, such as NO and CO_2, depress it.[1–3] Since N_2, CO_2, O_2, H_2, and NH_3 are well-known gases, it was therefore considered desirable to see the effect, if any, of irradiation atmosphere on protein reactions in N_2, CO_2, O_2, H_2, and NH_3.

The urea denaturation of protein was selected as the protein reaction, since it was described in a previous paper.[4] The determination can be followed conveniently by measuring the reduced viscosity of the solutions.

EXPERIMENTAL

Materials

N_2, CO_2, O_2, H_2, and NH_3 used in this work were a commercial materials. Albumin and urea used were the same as those preparations described in the previous paper.[4]

Apparatus and Procedure

The irradiation was from a 300-Ci^{60} Co source.

The dose rate in this work was 1.7×10^3 r/hr. Solid albumin was put into each irradiation bottle (Fig. 1), and gases were displaced with nitrogen, carbon dioxide, oxygen, hydrogen, or ammonia gas, and the irradiation was carried out at room temperature. The irradiated solid albumin was dissolved with distilled water and mixed with urea solution. Then the viscosity was measured.[4]

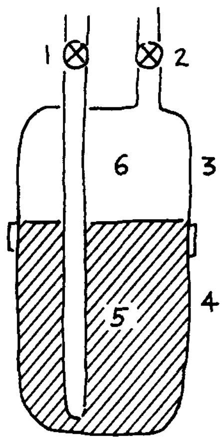

Fig. 1. Irradiation apparatus: (1,2) stop cocks; (3) cap; (4) body; (5) sample; (6) gas phase.

RESULTS

The viscosity change with time for the protein irradiated by γ-rays (10^3 r) in various atmospheres was studied with a 3% albumin in 10*M* urea at 30°C.

The gases used, i.e., N_2, CO_2, O_2, H_2, and NH_3, were selected because their dissociation energies E_d, resonance energies E_r, and the differences between dissociation and resonance energies are well known. These values are shown in Table I.

TABLE I
Gases Used in Irradiation of Solid Protein

Gas	Dissociation energy E_d, kcal/mole	Resonance energy E_r, kcal/mole	Energy difference ($E_d - E_r$), kcal/mole
N_2	225.1	0	225.1
CO_2	191.0	33	158.0
O_2	117.2	0	117.2
H_2	103.2	0	103.2
NH_3	92.0	0	92.0

Experimental results are shown in Figure 2. The relation between the values of the reduced viscosity at infinite time and the energy difference of the gases composing the irradiation atmosphere is shown in Figure 3. From this result it is clear that the reduced viscosity does not reach an infinite value, but approaches a limiting value. The increase of the reduced viscosity with the increasing energy difference of the gases composing the irradiation atmosphere indicates that the irradiation atmosphere does affect the denaturation reaction of protein.

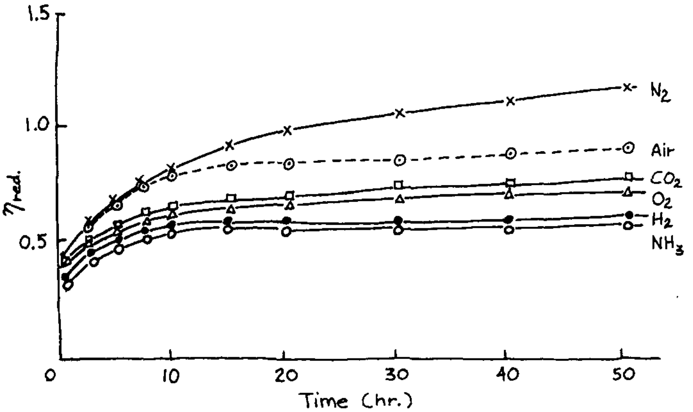

Fig. 2. Reduced viscosity–time curves in various irradiation atmospheres: 3% albumin in 10*M* urea; 10^3 r; 30°C.

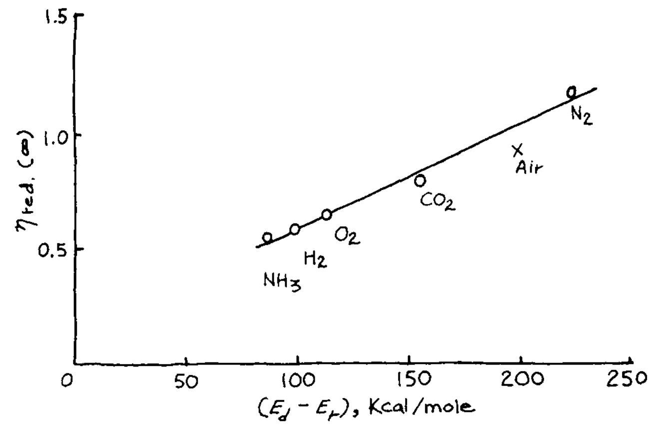

Fig. 3. Relation between reduced viscosity at infinite time and the energy difference of gas in the irradiation atmosphere.

DISCUSSION

It is well known that some gases, such as Xe, Kr, CO, and H_2O, accelerate the radiation effect in polymers while some other gases, such as NO and CO_2, depress it.[1–3]

In the present study, the protein reaction was estimated from the viscosity change (Figs. 2 and 3), the viscosity change in various irradiation atmospheres being related to the effect on the protein reaction of the energy difference of the gases composing the irradiation atmospheres. At constant concentrations of albumin and urea, an increase in energy difference results in an increase of activation energy required for the denaturation reaction. The reaction rate, therefore, depends on the energy difference for the gases composing the irradiation atmosphere. If the main mechanism for the activation reaction of protein is assumed to be as shown in eqs. (1)–(3):

$$\mathrm{P - P + X - X} \xrightarrow{h\nu} \mathrm{P^* + P^* + X^* + X^*} \tag{1}$$

$$\mathrm{X^* + X^* \rightarrow X - X} + (E_\mathrm{d} - E_\mathrm{r}) \tag{2}$$

$$\mathrm{P - P} \xrightarrow{(Ed - E_r)} \mathrm{P^* + P^*} \tag{3}$$

where P — P denotes protein molecule and X — X the molecule of gases composing the irradiation atmosphere, then the activation step is process (3), which means that the observed viscosity change is related to the energy difference ($E_\mathrm{d} - E_\mathrm{r}$) for the gases composing irradiation atmosphere. Therefore the response of albumin molecule to the irradiation atmosphere can be determined by measuring the reduced viscosity.

For the present system, E_d and E_r are the dissociation energy and the resonance energy per mole gas, and a' and c are adjustable constants; then one gets

$$\eta_{\mathrm{red}(\infty)} = a'(E_\mathrm{d} - E_r) + c$$

This formula agrees with the experimental data plotted in Figure 3.

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