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Radiation Chemical Studies of Protein Reactions: Effect of Sulfur-Containing Compounds on Optical Rotation

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ABSTRACT

Thiourea, thioglycol, and β,β'-thiodiglycolic acid were found to protect against changes in the internal relationships of the atoms in the protein molecule from radiation damage. The optical rotation behavior closely resembles that of amino acid which shows a similar dependence on concentration.

INTRODUCTION

It is well known that some sulfur-containing compound such as cysteine, cysteamine, gluthathione, and aminoethylisothuronium show a protective effect against radiation damage on biological macromolecule such as protein, nucleic acid, and hyaluronic acid [1-7].

Since thiourea, thioglycol, and β,β'-thiodiglycolic acid are well known S-containing compound, it was thought desirable to see whether

they show such a protective property and what the effect of their concentration would be on changes in the internal relationships of the atoms in the protein molecule.

The urea denaturation of protein was selected as the change in the internal relationships of the atoms in the protein molecule because it was described in the previous papers [8-9]. The determination can be conveniently followed by measuring the optical rotation of the solution as a function of the concentration of the S-containing compound.

EXPERIMENTAL

Materials

The albumin and urea used in this work were the same as those described in a previous paper [8]. The thiourea used was a commercial material produced by the Junsei Pure Chemicals Co., Ltd. The thioglycol used was a commercial material produced by the Tokyo Chemical Industry Co., Ltd. The β,β'-thiodiglycolic acid used was a commercial material produced by the Daiichi Pure Chemical Co., Ltd.

Apparatus and Procedure

An irradiation source containing about 1500 Ci of ^{60}Co was used. The dose rate in this work was 1.2×10^4 R/hr. The solid albumin was irradiated in air at room temperature. The irradiated solid albumin was dissolved with distilled water and mixed with the urea solution of the S-containing compound. Then the optical rotation was measured [9].

RESULTS

The changes with time in the optical rotation of albumin and S-containing compound (thiourea, thioglycol, or β,β'-thiodiglycolic acid) were studied with 2% albumin in 7 M urea, 10^3 R, and 30°C.

The results are shown in Figs. 1-3. The relation between the final specific rotation values and the percentage of S-containing compounds are shown in Fig. 4.

In the presence of the S-containing compounds the specific rotation of albumin solutions decreased in a linear fashion when a logarithmic abscissa for the concentration of the S-containing compounds in percent was adopted (Fig. 4). The slope of the lines in Fig. 4 depended upon the structure of the S-containing compounds.

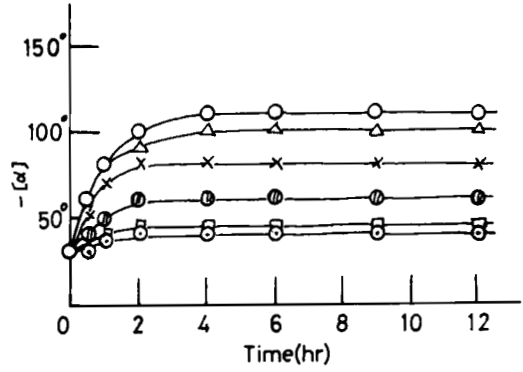

FIG. 1. Specific rotation vs time in the presence and in the absence of thiourea: (○) none, (△) 10^{-3}%, (×) 10^{-2}%, (⊕) 10^{-1}%, (□) 10%, and (⊙) 2 × 10%. Conditions: 2% albumin in 7 M urea, 10^3 R, and 30°C.

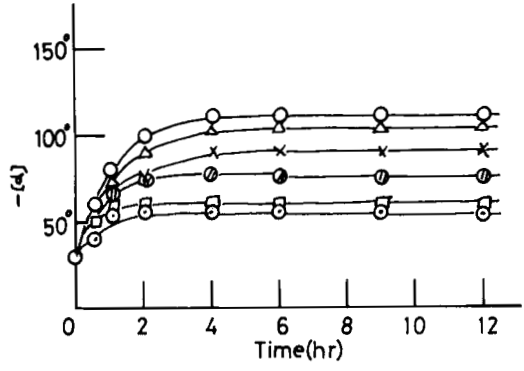

FIG. 2. Specific rotation vs time in the presence and in the absence of thioglycol: (○) none, (△) 10^{-3}%, (×) 10^{-2}%, (⊕) 10^{-1}%, (□) 10%, and (⊙) 2 × 10%. Conditions: 2% albumin in 7 M urea, 10^3 R, and 30°C.

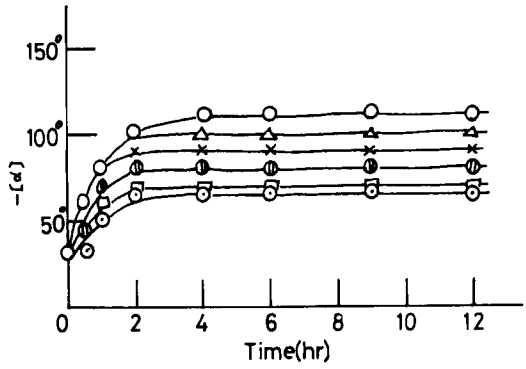

FIG. 3. Specific rotation vs time in the presence and in the absence of β,β'-thiodiglycolic acid: (○) none, (△) 10^{-3}%, (×) 10^{-2}%, (◍) 10^{-1}%, (□) 10%, and (⊙) 2×10%. Conditions: 2% albumin in 7 M urea, 10^3 R, and 30° C.

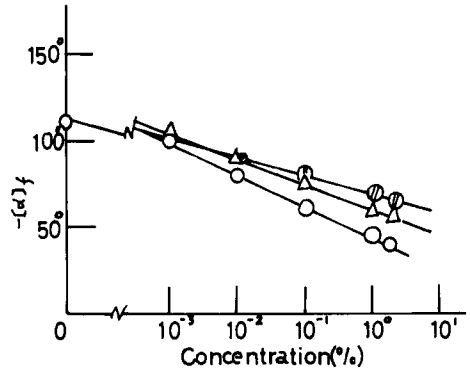

FIG. 4. Dependence of protective effect on the concentration of sulfur-containing compound: (○) thiourea, (△) thioglycol, and (◍) β,β'-thiodiglycolic acid. Conditions: 2% albumin in 7 M urea, 10^3 R, and 30° C.

From these it is clear that the effect of the S-containing compounds on the optical rotation is apparently related to their protective action on changes in the internal relationships of the atoms in the protein molecule. These effects are in the following order of concentration dependency: thiourea > thioglycol > β,β'-thiodiglycolic acid.

DISCUSSION

Changes in the internal relationships of the atoms in protein molecule were estimated from changes in the optical rotation as shown in Figs. 1-3. The relation between changes in optical rotation and the concentration of the S-containing compounds is related to changes in the internal relationships of the atoms in protein molecule.

When the concentrations of protein and urea and the radiation dose are all constant, a change in the concentration of the S-containing compounds results in a change in optical rotation required for the internal relationships of the atoms in protein molecule (see Fig. 4). This behavior indicates that the S-containing compounds protect against changes from radiation in the internal relationships of the atoms in the protein molecule. Since an increase in the concentration of the S-containing compounds in percent decreases the optical rotation of the protein molecule, the protection against changes in the internal relationships of the atoms in the protein molecule from radiation must be due to the presence of the S-containing compound.

At the concentration studied, this protection may be due to the interaction of the sulfur of the S-containing compounds with the activated group in the activated position in the vicinity of the asymmetric carbon atoms in protein molecule formed by radiation before they can attack the urea, or the sulfur may interact with either group in the protein molecule. The following processes were assumed for the protective reaction:

$$\text{P—P} \xrightarrow{h\nu} \text{P}^* + \text{P}^*$$

$$\text{P}^* + \text{S} \longrightarrow \text{P—S—P}$$

$$\text{P—S—P} \longrightarrow \text{P—P} + \text{S}$$

where P—P is the group in the initial position in the vicinity of the asymmetric carbon atoms in the protein molecule, P* is the activated group, S is the S-containing compound, and P—S—P is the linkage of the S-containing compound—group in protein.

For the present system the observed specific rotation is expressed in linear fashion by adopting a logarithmic abscissa for the concentration of the S-containing compound in percent:

$$[\alpha]f = b - a \log X$$

This formula agrees with the experimental data that describe the lines in Fig. 4. The concentration dependency is related to the structure of the S-containing compounds. This behavior of the S-containing compounds shows a similar dependence on the concentration as was found in earlier experiment [9].

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