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Influence of Pressure on the Reversible Unfolding of Ribonuclease and Poly- γ -benzyl-L-glutamate¹

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The effect of pressure on the thermal transitions of ribonuclease aqueous solution at pH 2.80 and of poly- γ -benzyl-L-glutamate (PBG) in dichloroacetic acid and 1,2-dichloroethane has been investigated to 1400 atm. by optical rotation measurements. An increase in pressure enhances unfolding for both ribonuclease and PBG. The pressure dependence on the extent of unfolding can be used to calculate the volume change for assumed basic steps of the transition process. For ribonuclease the volume change as calculated for a single-step reaction mechanism was found to be sufficiently smaller than that given by direct determinations of Holcomb and Van Holde, so that the reaction mechanism must consist of more than one reaction step. For the PBG transition an application of the helix-coil transition theory of Zimm, Doty, and co-workers, along with the measured pressure dependence upon the extent of transition, showed that the volume change of the process is at the experimental limit of direct determinations. The shift in the transition temperature with pressure for PBG was used to estimate a heat capacity change at constant pressure of approximately 140 cal./mole-deg. for the helix to random coil transition.

Introduction

Thermally induced transitions of macromolecular structures have been found for a variety of polymer materials.² The reversible transitions of ribonuclease³⁻⁶ and synthetic polypeptides⁷⁻¹⁰ have been the subjects of experimental and theoretical investigation. One of the primary purposes of such studies has been to gain insight into the mechanism of the transition process. In the case of ribonuclease, the strategy has been to interpret the extent of reaction as a function of temperature by assumed simple reaction mechanisms.

The heat of the assumed reaction may then be found from the dependence of the extent of reaction upon transition.¹¹ Until recently,¹² direct calorimetric meas-

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