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Rate Constants Measured for Hydrated Electron Reactions with Peptides and Proteins

The results of a study to measure absolute rate constants for reactions between the hydrated electron and peptides or proteins have been documented by Reinier Braams of Argonne National Laboratory, Argonne, Illinois. This basic knowledge may contribute to the understanding of mechanisms of chemical changes in biological systems.

In a protein, the amino acids are linked together through peptide bonds. Each protein molecule contains a large number of these bonds. Therefore, it is of considerable importance to know if the peptide bond introduces a reactive site involved in reactions with the hydrate electron. It was established that the peptide bond is *not* reactive toward the hydrated electron and that the reactivity of a problem can be ascribed to reactions with only a few specific amino acid side chains.

In this study of the effects of ionizing radiation on the amino acids of proteins, the reactivity of the protonated amino group is shown to depend upon the pK_a of the group. Estimates of the rate constants for reactions involving the amino acid side chains are presented. From the estimated rate constants for the side chains, an approximate rate constant for three different protein molecules has been calculated. In the linear gelatin molecule, the calculated value agrees well with the experimental value. For the ribonuclease and lysozyme, however, the calculated values differ from the measured values. The differences are ascribed to the influence of the protein charge on the encounter frequency, and to the effect of folding of the peptide chain on the effective collision radius of the molecule.

The proteins investigated have shown a high reactivity toward the hydrated electron. In order to

measure the absolute rate constants, low molar concentrations and small electron pulses were necessary. For this reason, the experiments were carried out with a multiple pass cell, allowing the analyzing light beam to pass through the radiation cell several times. Usually, eight passes were made, giving an optical path length of 32 cm in the protein solution. The radiation dose of 0.4- μ sec pulse was of the order of 500 rad and produced about 1.5 μ M of hydrated electrons. In some experiments with gelatin, the molar concentration was smaller than the initial concentration of hydrated electrons after one single pulse. The rate constant was then obtained from the initial slope of the decay curve after the first single pulse.

Notes:

1. A paper, entitled "Rate Constants of Hydrated Electron Reactions with Peptides and Proteins," *Radiation Research*, volume 31, no. 1, pp. 8-26, May 1967, Academic Press Inc., presents and analyzes the results of these measurements.
2. This work is of a fundamental nature and may be of interest to cell physiologists, medical researchers, biochemists, and biophysicists.
3. Inquiries concerning this innovation may be directed to:

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Reference: B68-10424

Source: R. Braams
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(continued overleaf)

Patent status:

Inquiries about obtaining rights for commercial use of this innovation may be made to:

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