

## CHAPTER II

### COMPETITION KINETICS STUDIES OF AMINO ACID AND NITRATE IONS

#### 2.1 Competition Kinetics Approach

Before direct kinetic techniques were adapted to studying the reactions of  $e_{aq}^-$ , the experimental approach used was that of competition kinetics, based on determining the yield of products after irradiated solutions containing scavengers reached equilibrium.

The basic mechanism of competition kinetics reaction is represented by two simple competing processes (1).



where A and B are substances which compete for radical R in solution;  $P_A$  and  $P_B$  are the corresponding products. The probability that radical R will react with substance A is given by the expression

$$\frac{k_A[A]}{k_A[A] + k_B[B]}$$

The radiation-chemical yields of the product formed,  $G(P_A)$  and of the reacting radical  $G_R$  can be expressed as

$$G(P_A) = G_R \frac{k_A[A]}{k_A[A] + k_B[B]} \quad \dots\dots\dots (3)$$

To get graphical representation this expression is transformed to

$$\frac{1}{G(P_A)} = \frac{1}{G_R} \frac{k_A[A] + k_B[B]}{k_A[A]} \dots\dots\dots (4)$$

$$= \frac{1}{G_R} + \frac{1}{G_R} \frac{k_B[B]}{k_A[A]} \dots\dots\dots (5)$$

This equation is of linear type. The slope is  $\tan \alpha$ , which is equal to  $\frac{1}{G_R} \cdot \frac{k_B}{k_A}$  and the intercept is  $\frac{1}{G_R}$ .

The competition plot for the relative rate constant determination is shown in Figure 2.1

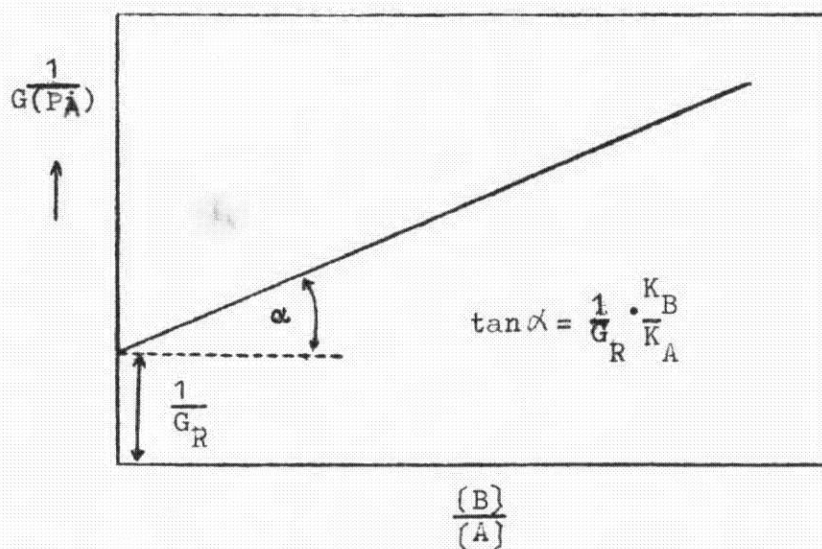


Figure 2.1 The competition plot used in the relative rate constant determinations.

## 2.2 The Amino Acid-Nitrate Ion System

In this particular work, the amino acid-nitrate ion system in deaerated aqueous solutions was chosen to investigate the kinetic behavior of  $e_{aq}^-$  and its precursor, using the competition method. Since it is already known that  $NO_3^-$  is a good  $e_{aq}^-$  scavenger, whereas amino acids are not (5), it is of interest to look at the effect of varying the concentration of amino acid on the yield of the final product,  $NO_2^-$ . It is thought that amino acids are more efficient scavengers of the precursor of the hydrated electron. If an increase in amino acid concentration causes a decrease in the yield of nitrite ion, it would imply that the yield of  $e_{aq}^-$  had also decreased according to the following reaction (6).



where S here stands for  $NO_3^-$ ,  $P_A$  for  $NO_2^-$  and  $R_A$  is the short-lived intermediate in the reaction. The electron could be scavenged in the earlier stages of irradiation, that is, before hydration, and it is probable that the prehydrated scavenger of  $e^-$  is the amino acid since nitrate ion is known to scavenge hydrated electrons efficiently. In addition,  $NO_3^-$  is also known to react with the prehydrated electron to some extent. In the presence of high concentrations of  $NO_3^-$  ion, the yield of  $e_{aq}^-$  may decrease because of scavenging of  $e_{dry}^-$ , together with  $e_{aq}^-$ , by  $NO_3^-$ .

The studies of competition reactions of solutes as scavengers for other free radicals, such as H or OH etc. give information about

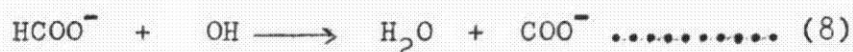
the effect of these scavengers on primary molecular yields such as  $H_2$  or  $H_2O_2$  obtained in water radiolysis. A number of studies have already been done (5)(6)(7)(8). However, in this work, the study is confined to the behaviour of the hydrated electron and its precursor. H and OH radicals were eliminated by the addition of sodium formate, an efficient scavenger for both radicals.

The reduction of nitrate to nitrite by hydrated electron (9) has been shown to proceed via the intermediate formation of the radical ion,  $NO_3^{-2}$ , according to the following reactions:

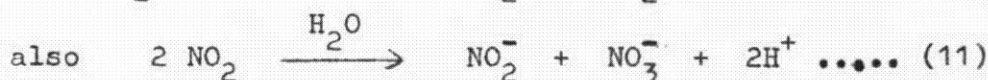
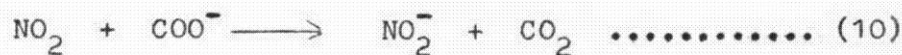


The  $NO_2$  formed can react further with other negative ions contained or produced in the solution to give nitrite ion,  $NO_2^-$ .

The solutions studied contains sodium formate which acts as hydroxyl scavenger in irradiated solution by the following reactions:

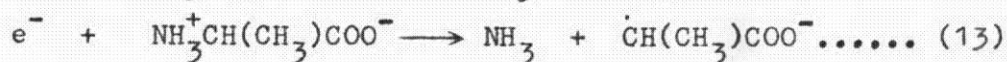
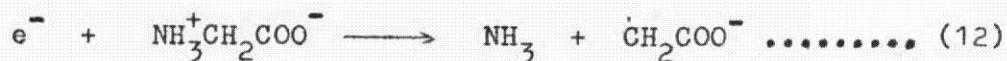


$COO^-$  ions react with  $NO_2$  molecules formed in equation (7) to give nitrite ion and carbon dioxide as products:



If the irradiated solution contains no other scavenger for the electron, either dry or hydrated, all  $e_{aq}^-$  will react with  $NO_3^-$  and yield of final product and  $G_{e_{aq}^-}$  itself would vary with  $[NO_3^-]$ . Since there is an observed effect of the amino acid concentration on the yield of hydrated electron, amino acids are assumed to attack electrons produced in the radiolytic processes. Since they have been shown to be poor scavenger for hydrated electron, it is suggested that they react with the hydrated electron precursor;  $e_{dry}^-$ .

The mechanism of electron reacting with amino acids can be represented (2) by:



For glycine the main products turn out to be ammonia, glyoxylic acid, acetic acid and hydrogen with smaller quantities of  $CO_2$ , formaldehyde, methylamine and formic acid. Alanine gives similar products; ethylamine, propionic acid, pyruvic acid and acetaldehyde instead of methylamine, acetic acid, glyoxylic acid and formaldehyde. However, the product of interest is nitrite reduced from nitrate which can be determined easily after the steady state has been reached in the solution.  $G(NO_2^-)$  is obtained from a spectrophotometric measurement and  $G_{e_{aq}^-}$  can be determined by simple calculation from the kinetic equation. The experimental techniques are described in details in chapter III.

2.3 This theory of prehydration scavenging of hydrated electron seems to contrast with the diffusion kinetic model described in previous chapter. In the diffusion kinetic model it has been assumed that all radicals and ions formed react only after thermalization and solvation of these species have been completed, therefore the prehydration scavenging of hydrated electron should take place before diffusion of species into the bulk. Thus this reaction of prehydrated electron should occur very rapidly. The evidence for this has not been observed directly in pulse radiolysis work and is still open to question. Any reaction occurring with dry electron would be completed in 0.1 - 10 picoseconds.

However, the present work was done to obtain more informations about the reaction of the electron with amino acids. The rate constants of the reaction of amino acid and  $e_{aq}^-$  were obtained and further support for the mechanisms have been derived.