CHAPTER V

DISCUSSION

5.1   The three competition graphs of glycine-nitrate system show similar trends, that is they are linear from the beginning until the ratio of glycine to nitrate exceeds a certain value, then they show curvature. This would seem to indicate that in the linear portion the simple mechanism of the two competing reactions is valid, whereas curvature indicates that a more complicated mechanism is involved. Similar results were obtained in the case of alanine-nitrate systems, but scattering of the points was greater in the glycine system.

The rate constants of the reaction of glycine and e_{aq}^- vary from 8.0×10^6 to 2.33×10^8. Those of alanine and e_{aq}^- vary from 5.04×10^7 to 1.08×10^8. Previous work reported by M. Ebert and A.J. Swallow (2) have concluded that the rate constant for reaction of e_{aq}^- with glycine is $8.5 \pm 0.5 \times 10^6$ $M^{-1}sec^{-1}$ and with alanine $6 \pm 1 \times 10^6$ $M^{-1}sec^{-1}$ However, Garrison and colleaques found that the value for alanine is about 20 times more than that of Ebert and Swallow. Therefore, the rate constant values in this present work are in the same range as others reported. It has to be borne in mind that relative rate constant determination method used here gives lower accuracy, compared to the direct method of pulse radiolysis. It is possible that the variation in the values of rate constant are

due to the change in ionic strength (μ). However, this effect should not be a large effect in this case since the difference in the values of ionic strenght is only about 0.0045 from the highest to the lowest concentration.

Increases of the concentration of glycine and alanine cause decreases in the yield of nitrite ion (Table 4.1 and 4.3). This was also reported by Draganic & Draganic. It is obvious that glycine and alanine affect the measured yield of nitrite. Although the absolute values of $G_0(NO_2^-)$ in this work are somewhat lower than those of Draganic and Draganic, but the trends observed in our measurements agree with their previous work (5)(7).

Discrepancy in the $G_0(NO_2^-)$ values occur because of the determination of nitrite. It was found in this work that the molar extinction coefficient varies with amino acid concentration. Therefore different values of ϵ were used at various amino acid concentrations; in previous work this correction was not made. Thus the actual values of $G_0(NO_2^-)$ measured in this work were lower. Also with higher concentrations of glycine there was a problem. It was found in this experiment that longer irradiation of the sample solutions caused precipitation at the time when the complex dye was formed in the analytical procedure for NO_2^-. To avoid this problem sample solutions were irradiated for a shorter period of time. Again, the formation of nitrite ions would be less in this case, giving a large experimental error in the nitrite absorbance values. However, at shorter irradiation times, the extrapolation for $G_0(NO_2^-)$ is likely

to give a more accurate value. Since it is known that as the time for irradiation increases $G(NO_2^-)$ will gradually increase to a certain extent then it will decrease again at longer irradiation time; there is the optimum value for $G(NO_2^-)$. Extrapolation will give high or low value of $G_0(NO_2^-)$, depending on which part of the graph obtained. The complete profile should be obtained. The low value is in fact the correct one. In this work low values of $G(NO_2^-)$ were obtained because it was necessary to use short irradiation times.

Alanine has a greater effect on the yield of nitrite than glycine. The $G_0(NO_2^-)$ values substantially decrease as the alanine concentrations increase.

The effect of absolute concentration of nitrate on $G_0(NO_2^-)$ is significant for both glycine and alanine for nitrate concentration ranging from 5×10^{-4} M to 5×10^{-3} M. The effect is highest at 1×10^{-3} M NO_3^- for glycine and at 5×10^{-4} M for alanine.

5.2   Yields of hydrated electron were calculated from the $G(NO_2^-)$ value, according to the following equation

$$G(e_{aq}^-) = G(NO_2^-) \left[1 + \frac{k_{e_{aq}^- + AA} \left[AA \right]}{k_{e_{aq}^- + NO_3^-} \left[NO_3^- \right]} \right]$$

The value of $G(NO_2^-)$, $[AA]$, $[NO_3^-]$ and $k_{e_{aq}^- + AA}$ came from the experimental work and calculations. The rate constant of hydrated electron with nitrate (1.1×10^{10} M^{-1} sec^{-1}) was taken from the literature (1) and is well established.
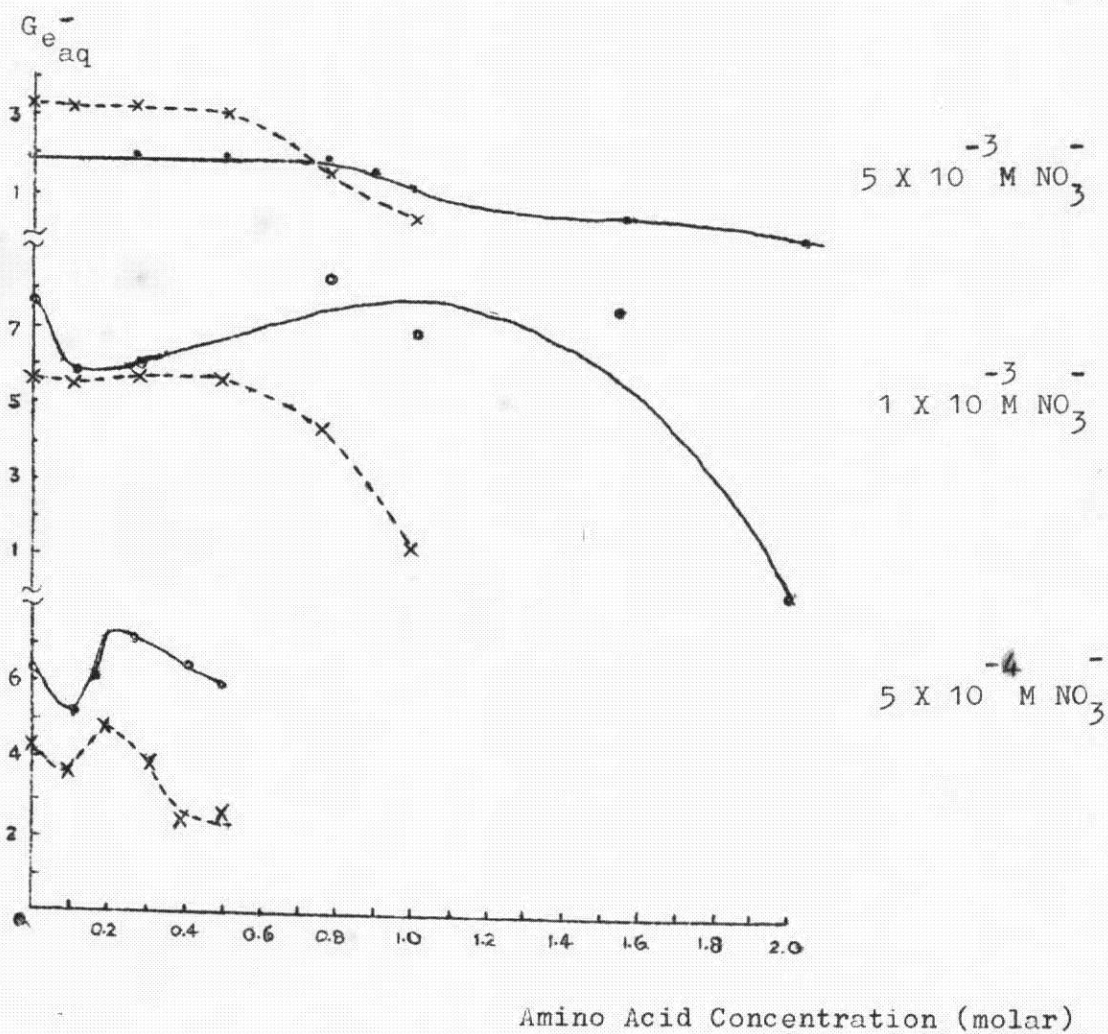
Figure 5.1 Plot of yield of hydrated electron as a

function of amino acid concentration

. = glycine

× = alanine

The graphs of $G_{e^-_{aq}}$ as a function of amino acid concentration are shown in Figure 5.1. The curves were compared with the Draganic' and Draganic's work (7). The absolute values of yield of hydrated electron were different but the trends of the graphs were similar to their work, i.e. at higher amino acid concentrations the yields of hydrated electron decrease. $G(e^-_{aq})$ at zero concentration of amino acid was obtained from the intercept of the competition plot. It is found that the yields of hydrated electron decrease at the very dilute concentrations of amino acid, ranging from 0 to 0.1 M, then they slightly increase and finally decrease again at higher concentrations. This interesting behavior was observed in three graphs, two from glycine and one from alanine. These might result from reaction of some products produced in the initial stage with electrons before the latter become hydrated. At higher concentrations the amino acids are more efficient and the mechanism can be explained by the prehydration scavenging assumption. For the highest absolute value of NO_3^-, 5×10^{-3}M, the graphs are smooth and there is no evidence of rapid reduction of the yield of hydrated electron. At this NO_3^- concentration alanine gives a low yield of hydrated electron $(G_{e^-_{aq}})$ at higher concentration of amino acid. At lower amino acid concentration, the yield of hydrated electron for alanine exceeds that of glycine. The other two pairs of graphs for lower values of NO_3^-, 1×10^{-3}M and 5×10^{-4}M show a greater difference in relative values between glycine and alanine. These observations support the results from previous work that alanine has more effect on the yield of hydrated electron than glycine.

In addition, the results of this experimental work agree
with the hypothesis of Hamill et al (4) that amino acids can react
with the precursor of hydrated electron, i.e., dry electron which
are present in the solution before hydration occurs. Decreases in
yields of hydrated electron as the amino acid concentrations
increase implies that prehydration scavenging of electron takes
place in the solution. Similarly, at higher concentration of
nitrate it was found that $G(e_{aq}^-)$ substantially decreases. It is
not in doubt since NO_3^- is a good scavenger for e_{aq}^-. The rate con-
stant of the reaction of nitrate with e_{aq}^- is higher than those of
alanine and glycine, i.e. about 10^3 times for glycine and 10^2 times
for alanine. Therefore both glycine and alanine have lower re-
activities towards e_{aq}^- than nitrate. The rate constants of glycine
and alanine are not diffusion-controlled because they are less than
$10^{10} M^{-1} sec^{-1}$. A quantitative examination of the rate constant data
for diffusion-controlled processes compared with that of e_{aq}^- re-
actions reveals however that most of the latter reactions with
specific rates of $< 10^{10} M^{-1} sec^{-1}$ are not diffusion-controlled. The
parameters used in diffusion-controlled reactions are a diffusion
coefficient of about $10^{-4} sec^{-1}$ and an effective radius of 2.5 - 3.0 A°
according to Debye's theory.

The data obtained in this work does not provide conclu-
sive evidence about the reactivity of glycine and alanine towards
e_{aq}^- and its precursor. However, what can be drawn from the results
is that amino acid (glycine or alanine) is a poor scavenger for

e_{aq}^- and the rate constants obtained agree well with this theory.

Curvature shown in the competition graphs at higher con-
centrations implies more complicated mechanisms which might due to
further reactions involving some products from the reactions of
electron with glycine or alanine. These products may react further
with e_{dry}^- or e_{aq}^- as competing scavengers. Thus the mechanisms can
not be explained just by the simple kinetic equation. More work
should be carried out on the behavior of the products obtained in
the reaction with respect to electrons produced in the radiolysis.

The discovery of the hydrated electron in irradiated
aqueous solutions has made it necessary to re-examine the mechanisms
proposed for the irradiation of aqueous solutions of substances
which are biologically important. The new technique of pulse
radiolysis are required particularly in determination of absolute
rate constants and in the observation of reaction intermediates for
determining the reaction mechanisms. In the case of alanine and
glycine reacting with dry electrons, the reactions occur at faster
time scales than can be measured at present.

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