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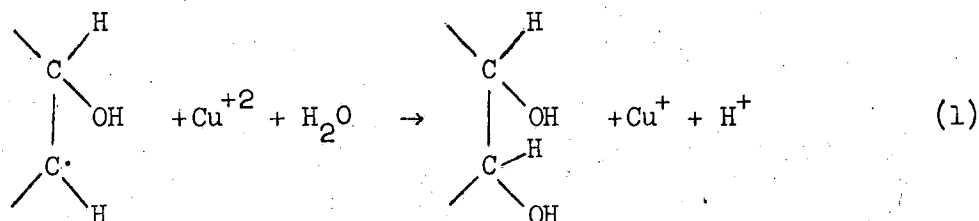
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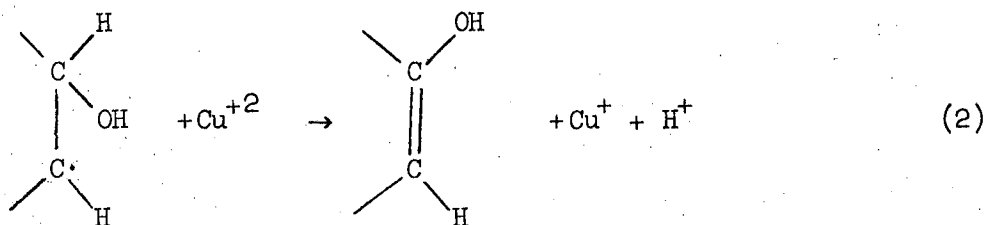
The chemical evidence is that both the hydrated electron, e_{aq}^- , and the hydroxyl radical, OH, which are formed as the principal intermediates in water radiolysis, react rapidly with the pyrimidine bases through preferential addition to the 5, 6 double bond to give the hydroxypyrimidyl radical, BH, and the hydroxypyrimidyl radical, BOH, respectively.¹⁻⁴ The yields for base destruction (molecules/100 eV) in oxygen-free solutions under γ -rays are, however, consistently low, $G(-B) \leq 1$,⁵⁻⁶ when compared to primary yields of the radical species derived from water, $G_{e_{\text{aq}}^-} = 2.85$, $G_{\text{OH}} = 2.9$;⁷ recent work indicates that secondary reactions of BH and BOH lead to regeneration of the parent compound.⁴ In oxygen-saturated solutions, e_{aq}^- is scavenged by O_2 to form $\text{O}_2^-(\text{HO}_2)$, the regeneration reaction is quenched, and the yield for base destruction increases to $G(-B) \sim 2$ through reactions involving the peroxy radical, $\text{B}(\text{OH})\text{O}_2$. However, a multiplicity of organic products are formed in the removal of the intermediate, $\text{B}(\text{OH})\text{O}_2$, and the overall product stoichiometries are yet to be fully elucidated.⁸

We find that the use of a transition metal ion such as Cu^{+2} and Fe^{+3} in the place of molecular oxygen as a scavenger of intermediate radicals leads to a considerable simplification in the radiation chemistry of aqueous solutions of the representative bases, uracil and cytosine. The specific chemical effects of Cu^{+2} in these systems involve the preferential oxidation of the hydroxypyrimidyl

radicals to give the corresponding glycols as the principal products of radiolysis



as evidenced by the data of Table I for both uracil and cytosine. Formation of the isobarbituric acid derivatives (5-hydroxypyrimidines) with $G \leq 0.5$ in each case may be attributed to a parallel branching reaction



Hence, in the presence of Cu^{+2} the pyrimidine nucleus is quantitatively oxidized in accord with the stoichiometry $G(1)+G(2) \approx G_{\text{OH}} = 2.9$. Reactions akin to steps 1 and 2 have been observed in other systems.⁹⁻¹¹

The velocity constants for reaction of e_{aq}^- with $\text{Cu}^{+2(12)}$ and with the pyrimidine bases¹³ are such that at the low $[\text{base}]/[\text{Cu}^{+2}]$ ratios of Table 1, capture of e_{aq}^- is predominantly by $\text{Cu}^{+2} + e_{\text{aq}}^- \rightarrow \text{Cu}^+$. However, at the higher $[\text{base}]/[\text{Cu}^{+2}]$ values, e_{aq}^- is scavenged almost exclusively by the base. Such reaction does not lead to net chemical change in the base since reaction of the hydropyrimidyl radical, BH , with Cu^{+2} via $\text{BH} + \text{Cu}^{+2} \rightarrow \text{B} + \text{Cu}^{+2} + \text{H}_2\text{O} \rightarrow \text{BH}(\text{OH}) + \text{Cu}^+ + \text{H}^+$, $\text{BH}(\text{OH}) \rightarrow \text{B} + \text{H}_2\text{O}$ leads to base regeneration.

In the present experiments, the glycol and isobarbituric acid derivatives were separated from the parent compounds and from Cu^{+2} by chromatography on Dowex-50

ion-exchange resin (hydrogen form). Aliquots of the irradiated solutions were placed directly on the column and in the case of uracil, the product species were fractionally eluted with water. Product separation in the case of cytosine was effected with dilute hydrochloric acid² at gradually increasing concentrations over the range 0 to 2N. The yield of 4-amino-isobarbituric acid from cytosine and of isobarbituric acid from uracil were calculated on the basis of $\epsilon_{300\text{m}\mu}$ = $5.4 \times 10^3 (\text{pH} < 1)^2$ and $\epsilon = 6.6 \times 10^3 (\text{pH} < 1)^{14}$ respectively. Fractions containing cytosine glycol and uracil glycol were heated in 2N HCl after the method of Ekert and Monier² to quantitatively convert those products to the isobarbituric acid forms for assay.

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Table 1

Product yields in the γ -radiolysis of Pyrimidine-Cu⁺² solutions.

	<u>Base (mM)</u>	<u>Cu⁺² (mM)</u>	<u>pH</u>	<u>G(glycol)</u>	<u>G(isobarbituric)</u>	<u>ΣG(Products)</u>
uracil	30	2	5	2.3	0.50	2.8
	30	1	5	2.3	0.60	2.9
	30	0.5	5	2.3	~0.7	3.0
	10	10	3.5	2.4	0.45	2.85
cytosine	10	2	3.7	2.28	0.42	2.70
	20	1	3.1	2.25	0.45	2.70

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