SHORT COMMUNICATION

Flash Photolysis Study of Reaction between Thymine Glycol and Hydrated Electron

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ABSTRACT

The reaction between thymine glycol and hydrated electron was studied by the flash photolysis technique with a time resolution of 10 μsec. Hydrated electron was formed from ferrocyanide ion in the aqueous solution of thymine glycol. Though its lifetime was shorter than the time resolution of measurements, the rate constant was estimated to be $>2.8 \times 10^9$ M$^{-1}$·sec$^{-1}$ at 19°C from the yield of hydrated electron as a function of the concentration of thymine glycol present. The high rate constant explains the results from a conventional scavenger method.

During the course of radiation chemical studies of aqueous solution of thymine, it was found that thymine glycol, the product of the reaction between thymine and hydroxy radicals, reacts readily with hydrated electron to restore thymine.1) The rate constant of this reaction was recently found to be as high as $2.8 \times 10^9$ M$^{-1}$·sec$^{-1}$ by the conventional scavenger method.2) However, it may be worth while confirming the high rate constant more directly to reveal the elementary processes of this reaction. From this point of view, the flash photolysis study was carried out for the aqueous solution of potassium ferrocyanide with and without thymine glycol to study the reaction between hydrated electron photochemically ejected from ferrocyanide ion and thymine glycol. Matheson et al. studied the formation of the hydrated electron in the flash photolysis of aqueous solution of potassium ferrocyanide.3)

Synthesis and purification of thymine glycol was already reported elsewhere.4) Potassium ferrocyanide of reagent grade was used without further purification. Thymine glycol and potassium ferrocyanide were dissolved in triply distilled water and degassed by freezing-pumping-thawing method. Sample solution in a quartz cell (1 cm diameter $\times$ 10 cm long) was subjected to photolysis. Two flash lamps...
(15 cm long) connected in series were operated at 12 KV and 2 μF. Analyzing light from a Xe lamp (500 Watts) through the cell was monitored by a monochrometer (Shimadzu, GE-100) and a photomultiplier (EMI 6256 B). Occasionally, photographic method was used to examine the transient absorption spectra.

When the solution of 0.2 mM of potassium ferrocyanide is photolized, the photographic measurements reveal a transient absorption spectrum with a maximum at about 620 nm extending very widely. This absorption is attributed to hydrated electron. Fig. 1 (curve A) shows the time profile of the transient absorption monitored at 580 nm. Curve B shows the oscilloscope trace with the analyzing light off. The downward deflection is caused by the scattered flash light and, therefore, shows its time profile. The half-width of the flash light is 16 μsec. If one compares the shape of curve A with that of curve B, it may be obvious that the transient concentration of the hydrated electron appears to follow the intensity of the light and that the lifetime of the hydrated electron is shorter than the half-width of the light, 16 μsec. The short life of the hydrated electron is thought to be due to the competing reactions,

\[ e^{-} + e^{-} \rightarrow H_2 + 2OH^- \] and \[ e^{-} + Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{4-}. \]

When a small amount of thymine glycol is added to the solution, the transient absorption due to the hydrated electron decreases in its intensity under the other conditions unchanged. This is illustrated in Fig. 2, where the reciprocal of optical density at the transient peak absorption appears to increase linearly with the increasing concentration of thymine glycol. The optical densities were plotted after the correction of the contribution from the scattered flash light. The decrease in the concentration of the hydrated electron is not due to the masking effect of thymine glycol on the photolysis of ferrocyanide ion, because the UV absorption spectrum of the former is much weaker and lies in shorter wavelength region than the spectrum of the latter. Therefore, it is reasonably attributed to the additional path for the disappearance of the hydrated electron:

\[ e^{-} + \text{thymine glycol} \xrightarrow{k} \text{product} \]
FLASH PHOTOLYSIS OF THYMINE GLYCOL

If one denotes the lifetime of the hydrated electron by \( \tau \) and \( \tau_0 \) in the presence and in the absence of thymine glycol, respectively, they are related with each other as

\[
1/\tau = 1/\tau_0 + k \text{[thymine glycol]}
\]

(2)

The steady-state concentration of the hydrated electron during the photolysis is proportional to both its lifetime and the instantaneous light intensity, when \( \tau \) is enough shorter than the half-width of the flash light. Therefore, the peak value of optical density of the hydrated electron should follow the relation,

\[
1/\text{OD} = \text{const} \left( 1/\tau_0 + k \text{[thymine glycol]} \right)
\]

(3)

The linear dependence observed in Fig. 2 agrees with this prediction. If \( \tau_0 \) were to be comparable to or longer than 16 \( \mu \text{sec} \), the difference in shape should be observed between curve A and B in Fig. 1, with a tailing for the former curve. However, no difference was observed. The difference, if any, might be observable under the present experimental conditions, by examining the half-width of both curves, even if it was as small as 10\%. If one assumes safely that \( \tau_0 \) is shorter than 20\% of the half-width of flash light (3.2 \( \mu \text{sec} \)), the rate constant is estimated as \( k \geq 2.6 \times 10^9 \text{M}^{-1} \text{sec}^{-1} \) from the indication in Fig. 2 that \( 1/\tau_0 = k \text{[thymine glycol]} \)

for (thymine glycol) = 0.12 mM.

In the present study, \( k \) is not uniquely determined but the lowest limit is given for it. However, \( k \) cannot be much larger than \( 2.6 \times 10^9 \text{M}^{-1} \text{sec}^{-1} \), because the given limit is close to the rate constant of the diffusion-controlled reaction of hydrated electron, \( 10^9 \text{M}^{-1} \text{sec}^{-1} \). The result supports the rate constant determined by the conventional scavenger method for the reaction between thymine glycol and the hydrated electron\(^9\), and provides a direct evidence that this reaction is very rapid. It is, therefore, important in the radiation chemistry of aqueous solution of thymine, because the reaction between thymine and hydroxy radical may result in the formation of thymine glycol and show the rate constant in the same order of magnitude.\(^4\)

REFERENCES


