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AN INITIAL INTERMEDIATE ON PULSED ELECTRON IRRADIATION OF AQUEOUS SOLUTIONS OF MERCURIC IODIDE

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HgI_2 was found to react rapidly with e^-_{aq} producing initially a very short-lived intermediate with an absorption maximum at 470 nm. It decays via first order kinetics with a half-life of 1 μs to form another transient, HgI, absorbing at 360 nm. The first intermediate is proposed to be an e^-_{aq} or an H atom adduct.

Pulse radiolysis of aqueous Hg(II) solutions has been investigated by some workers,$^{1-6)}$ where HgX_2 (X = Cl, CN, etc.) is reduced by the e^-_{aq} or the H radical to form an unstable species, such as HgX, in the primary step. It was also revealed by laser flash photolysis of aqueous HgI_2 solutions$^{7)}$ that a transient absorption with a maximum at 340 nm was primarily formed, which could be attributed to HgI.

On pulsed electron irradiation of HgI_2 solutions, however, a short-lived intermediate of another type, probably a precursor of HgI, was found immediately after the pulse. The present report describes some natures of this intermediate.

The experimental details of pulse radiolysis measurements have been described previously.$^{2)}$ The shape of the pulse used was approximately triangular with a half width of ∿0.8 μs. Analysing light was obtained from a 500 W xenon lamp. HgI_2 was dissolved into triply distilled water through a sintered glass filter at room temperature. The concentration was determined on a spectrophotometer at 320 nm in solutions containing 0.1 M I^- ions, where Hg(II) exists in the form of HgI_4^{2-}.

Figure 1 shows absorption spectra at various times after the peak of the pulse obtained in a deaerated aqueous solution of 100 μM HgI_2 and 10 mM *t*-BuOH. An extremely short-lived intermediate with a broad absorption band around 470 nm is found immediately after the pulse. Concurrently with its decay, another absorption around 360 nm increases. The second intermediate also disappears via a second order rate law, $2k/\varepsilon^{360} = 2.0 \times 10^6$ cm s^{-1}, giving a residual absorption at shorter wavelengths. Small decrease of all the absorptions was observed in the solution without *t*-BuOH.

while N_2O-saturation of the solution suppressed most of these absorptions.

The radiolysis of water may be described by

$$H_2O \rightsquigarrow e^-_{aq},\quad H,\quad OH,\quad etc. \qquad (1)$$

the yields of the products being $G(e^-_{aq}) = 2.7$, $G(H) = 0.6$, and $G(OH) = 2.8$, respectively.[8)] Since the OH radical is entirely scavenged by *t*-BuOH in this system,[9)] the two intermediates are accepted to result from the reduction of HgI_2 mainly by the e^-_{aq}. This is supported by the result obtained in a solution saturated with N_2O that reacts rapidly with the e^-_{aq}.[10)] Contribution of the t-$\dot{B}uOH$ radical to these absorptions can be excluded from the comparison of the results obtained in the presence and the absence of *t*-BuOH, respectively. The small decrease of the absorption in the latter case is explained by the loss of the e^-_{aq} and possibly the reduced products of HgI_2 through their reactions with the unscavenged OH radical.

In view of the result reported by Jungbluth et al.,[6)] the second species may reasonably be regarded as HgI in consideration of the absorption spectrum and the decay constant. The residual absorption may also be explained by Hg_2I_2 resulting probably from the recombination of HgI. These assignments do not contradict the results of laser flash photolysis.[7)] On the other hand the first intermediate appearing at 470 nm is of another type which has never been found in the analogous systems. As is shown in Fig. 2a, the 470 nm-absorption decays rapidly only at the early stage. The slow component may be due to the second intermediate. The kinetic analysis was carried out on this consideration; the absorption at 7 μs after the pulse was used to calculate D_∞. Figure 2b shows that the decay of the first intermediate follows well the first order rate law, irrespectively of the pulse dose over about threefold range ($k = (8.3 \pm 0.5) \times 10^5\ s^{-1}$). An examination into the change of the absorption spectra during the early stage suggests that the 470 nm-species may be a precursor of HgI absorbing at 360 nm.

Similar results were obtained in acidic solutions containing $HClO_4$ up to 1 M, though the absorption yield at 470 nm was considerably smaller than that obtained in the neutral solution. The difference in the absorption yields between the two systems increased with decreasing HgI_2 concentration. In the acidic solution the H radical should play a role as a sole reducing agent, since the e^-_{aq} is converted to the H radical by the rapid reaction with the proton.[11)]

No spectral shift was found within experimental errors between the neutral and the acidic solutions. The smaller yield in the latter may well be explained by the decay during the pulse when the H radical reacts more slowly with HgI_2 than the e^-_{aq}

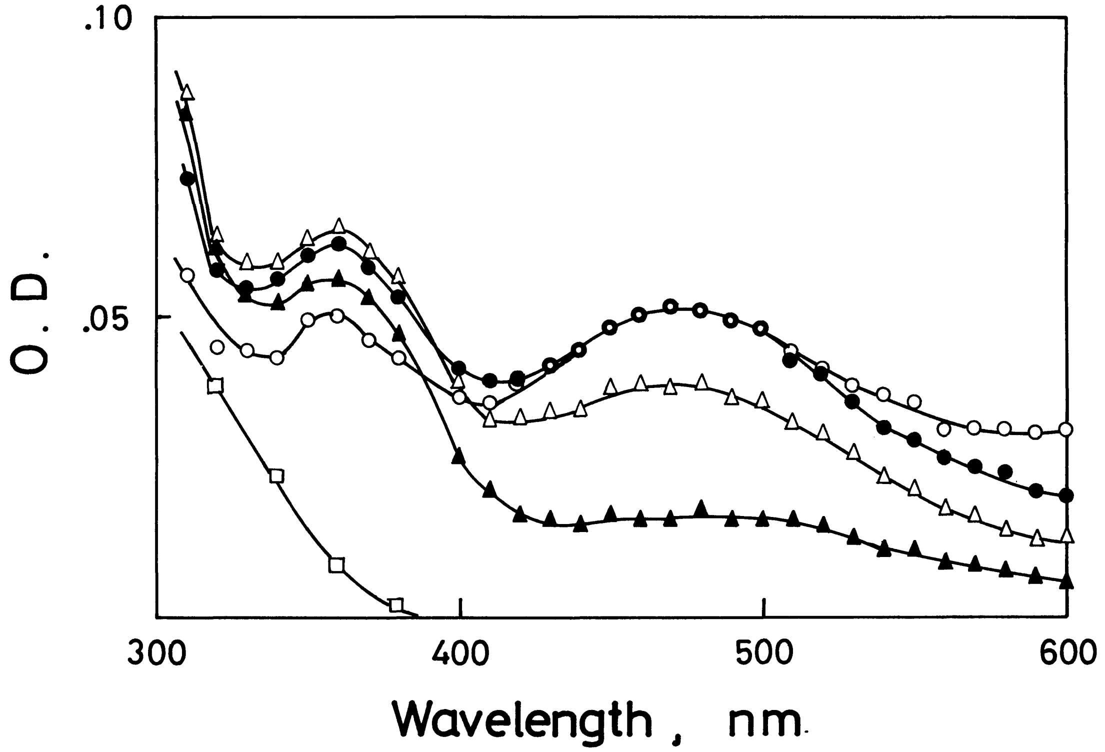

Fig. 1. Transient absorption spectra at various times after the peak of the pulse: ○, at the peak; ●, 0.3 μs; △, 0.8 μs; ▲, 2.3 μs; □, 150 μs; average dose, 2.8 krads.

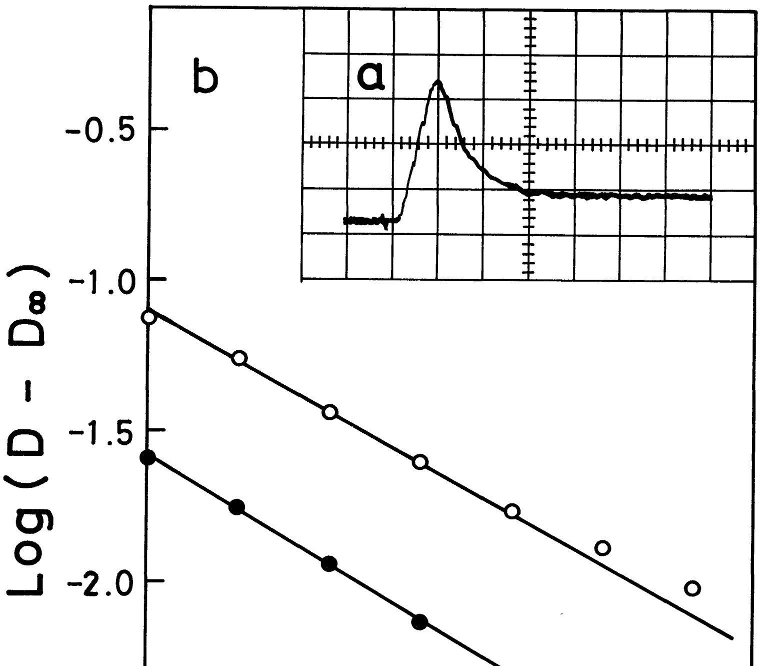

Fig. 2. (a) Oscilloscope trace of the transient absorption at 470 nm: dose, 1.71 krads; ordinate, 2.25 %/div.; absissa. 2 μs/div.
(b) First order plots for the decay of the first intermediate observed at 470 nm: ○, 5.02 krads; ●, 1.71 krads.

does. Such cases are generally found. For example, $HgCl_2$ reacts three or four times faster with the e^-_{aq} than with the H radical.[1, 12, 13]

It may be proposed on the experimental evidence that the first intermediate is assigned to a hydrogen or an electron adduct, which is a precursor of HgI.

$$e^-_{aq} \text{ or } H + HgI_2 \longrightarrow (HgI_2)_{e^-_{aq} \text{ or } H} \qquad (2)$$

$$(HgI_2)_{e^-_{aq} \text{ or } H} \longrightarrow HgI + I^- \text{ (or HI)} \qquad (3)$$

Considering the decay during the pulse the lower limit of the absorption coefficient was estimated to be 5500 M^{-1} cm^{-1} from the absorption quantities at the doses lower than $\sim 10^3$ rads in a deaerated aqueous neutral solution of 100 μM HgI_2 and 10 mM *t*-BuOH. Further investigations in the same system are being carried on.

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