Pulse Radiolysis of $HgBr_2$ in Aqueous Solutions

Shin-ichi Fujita, Hideo Horii, Toshiaki Mori, and Setsuo Taniguchi
Radiation Center of Osaka Prefecture Shinke-cho, Sakai, Osaka 593

(Received November 20, 1975)

Pulse radiolysis of aqueous $HgBr_2$ solutions was investigated in the range from visible to 260 nm. $HgBr_2$ is reduced by e_{aq}^-, H, CO_2^-, and some alcohol radicals except *t*-butyl alcohol radical to yield a transient species, HgBr, having an absorption spectrum with a maximum at 350 nm ($\varepsilon^{350}=(4.3\pm0.2)\times10^3\ M^{-1}\ cm^{-1}$). $k(e_{aq}^-+HgBr_2)$ was determined by the pseud-first order decay of e_{aq}^- observed at 500 nm as $(4.0\pm0.3)\times10^{10}\ M^{-1}\ s^{-1}$. The reactivities of the other reducing species toward $HgBr_2$ were estimated to be in the order $e_{aq}^- > CO_2^- > \dot{\mathrm{E}}\mathrm{tOH} \approx i\text{-}\dot{\mathrm{P}}\mathrm{rOH} > \mathrm{MeOH}$ by comparing the absorption yields of HgBr in equimolar $HgBr_2$ solutions containing the parent substances of the respective species. HgBr was found to decay following a second order rate law ($2k=(1.0\pm0.1)\times10^{10}\ M^{-1}\ s^{-1}$), producing Hg_2Br_2. $HgBr_2$ reacts also with the OH radical to give a transient species which shows a similar spectrum to that of Br_2^-. It is considered that the transient may be $HgBr_3$ instead of Br_2^-.

Pulse radiolysis of aqueous solutions of various mercuric salts has recently been investigated in order to find unstable mercurous species[1,2] and to clarify their behavior before they fall into the stable state.[3,4] It was found that the mercurous species behave in different ways depending on the pair anions attached. The results obtained for aqueous of mercuric bromide are described in the present report.

Experimental

Details of pulse radiolysis measurements have been described previously.[2,3] The dose per pulse was controlled by changing the pulse duration ($\lesssim 1$ μs) and the thickness of aluminum plate situated between the reaction cell and the outlet of the beam. With a thickness of 1—3 mm the delivered doses to the cell depended linearly on the coulomb values monitored by the system.[2] The light source used was a 500 W xenon lamp. All the solutions were prepared with guaranteed reagents and triply distilled water.

Results and Discussion

The spectra were obtained in a deaerated aqueous solution of 500 μM $HgBr_2$ containing 10 mM *t*-BuOH on irradiation with about 1 μs electron pulses (Fig. 1). The immediate absorption after the pulse has a peak at 350 nm. It decays rapidly following a second order rate law. Concurrently with the decay of the transient a residual intense absorption appears at shorter wavelengths within about 100 μs. Most of these absorptions were reduced by saturation of N_2O.

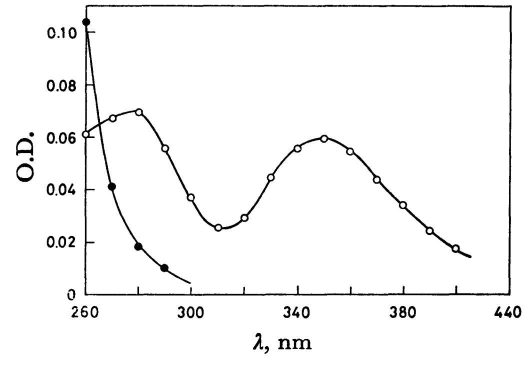

Fig. 1. Absorption spectra obtained in an deaerated aqueous solution of 500 μM $HgBr_2$ and 10 mM *t*-BuOH, immediately (○) and 100 μs (●) after the pulse; average dose, 2500 rad.

Irradiation of water with electron pulses produces the e_{aq}^-, H and OH radicals as reactive species. The OH radical is, however, scavenged by *t*-BuOH.[5] Since N_2O is known to react rapidly with the e_{aq}^-,[6] it is expected that the initial absorption is due to Hg(I) resulting from reduction of $HgBr_2$ by e_{aq}^-, the residual one being due to its dimer, $Hg_2(I)$.

$$e_{aq}^- + HgBr_2 \longrightarrow Hg(I) \tag{1}$$

$$Hg(I) + Hg(I) \longrightarrow Hg_2(I) \tag{2}$$

By observing the life time of e_{aq}^- at 500 nm in the range 10—30 μM $HgBr_2$, the rate constant, $k(e_{aq}^-+HgBr_2)$, was determined to be $(4.0\pm0.3)\times10^{10}\ M^{-1}\ s^{-1}$.

Entirely similar spectra were found in a deaerated 500 μM $HgBr_2$ solution with 10 mM *t*-BuOH at pH 2 where e_{aq}^- was converted into the H radical by the reaction with H^+.[7] It is accepted, therefore, that the H radical also reduces $HgBr_2$ rapidly.

$$H + HgBr_2 \longrightarrow Hg(I) \tag{3}$$

In the presence of other OH scavengers, such as formate ion, methanol, ethanol, and 2-propanol, additional growth curves appeared. Consequently the total absorption yields at 350 nm increased up to nearly twice as much as that in Fig. 1 in the case of formate ion as a scavenger. The resultant absorption spectra in these systems were also similar to those shown in Fig. 1. These results were not influenced essentially by saturation of N_2O in solutions.

Thus, it seems that the OH radical contributes to the reduction of $HgBr_2$ through its reaction products with scavengers.

$$OH + HCO_2^- \longrightarrow CO_2^- + H_2O \tag{4}$$

$$CO_2^- + HgBr_2 \longrightarrow Hg(I) + CO_2 \tag{5}$$

$$OH + ROH \longrightarrow \dot{R}OH + H_2O \tag{6}$$

$$\dot{R}OH + HgBr_2 \longrightarrow Hg(I) + \text{aldehyde or ketone} \tag{7}$$

where Reactions 4 and 6 are known to be very fast.[8,9] $k(CO_2^-+HgBr_2)$ was found to be $9\times10^9\ M^{-1}\ s^{-1}$ from the formation curve of the Hg(I) absorption at 350 nm. This value should, however, be accepted as an upper limit because, owing to its fast decay, Hg(I) could not attain the full equivalent for the CO_2^- yield. Thus,

TABLE 1. TRANSIENT ABSORPTION YIELDS IN DEAERATED AQUEOUS SOLUTIONS OF 0.87 mM $HgBr_2$ CONTAINING VARIOUS OH-SCAVENGERS AT A DOSE OF 2700 rad

Scavengers	$O.\,D._{max}$	$O.\,D._{relative}$[a)]
HCO_2Na	0.103	1.0
i-PrOH	0.092	0.89
EtOH	0.090	0.87
MeOH	0.065	0.63

a) Normalized to the value for HCO_2Na.

as to similar reactivities of some alcohol radicals, the order among each other was determined on the basis of the observed Hg(I) yield. Table 1 gives the maximum optical densities of the absorptions obtained in solutions of 0.87 mM $HgBr_2$ containing 10 mM respective alcohols or the formate ion at a dose of 2700 rad. Each maximum optical density should depend on the formation rate constant, k_5 or k_7, since the Hg(I) absorption decays rapidly at almost a uniform rate under these conditions. The values relative to the one for the formate ion are listed in the third column of Table 1. The results and the kinetic data show that the reactivities toward $HgBr_2$ are in the order $e_{aq}^- > CO_2^- > \dot{\mathrm{E}}\mathrm{tOH} \approx i\text{-}\dot{\mathrm{P}}\mathrm{rOH} > \mathrm{MeOH}$.

In a *t*-BuOH contained solution of 0.87 mM $HgBr_2$, a linearity of the absorption quantities *vs.* dose per pulse was obtained up to *ca.* 3000 rad. From the slope of the line the absorption coefficient of Hg(I) was calculated to be $\varepsilon^{350}=(4.3\pm0.2)\times10^3\ M^{-1}\ cm^{-1}$ on the basis of $G(\mathrm{Hg\ (I)})=G_H+G_{e_{aq}^-}=3.3$.

The results of the tests of a second order rate law for the decay of the transient at 350 nm at different doses in $HgBr_2$ solutions containing various OH-scavengers are given in Fig. 2. All the plots are linear, their slopes $(=2k_2/\varepsilon l)$, giving the same value of $(1.6\pm0.1)\times10^6\ s^{-1}$ for all the scavengers except *t*-BuOH. Thus, $2k_2=(1.0\pm0.1)\times10^{10}\ M^{-1}\ s^{-1}$ ($l=1.5$ cm). The rate constant was not affected by ionic strength of the solutions. The transient might be assigned to HgBr with no charge.

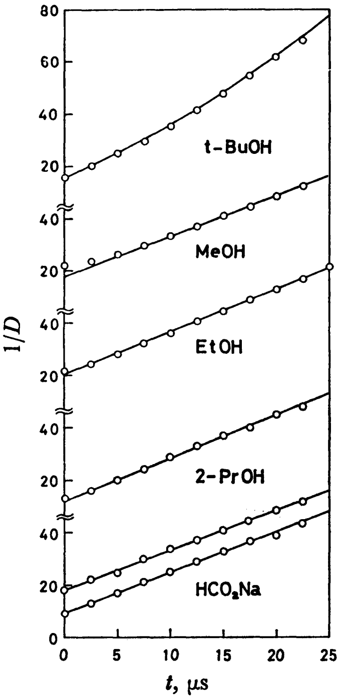

Fig. 2. Test of second order kinetics for the decay of Hg(I) at 350 nm in the presence of various OH-scavengers: $[HgBr_2]=500\ \mu M$, [scavenger]$=10$ mM; dose, ranging between 1300—2700 rad. In the case of HCO_2Na the dose giving the lower result is as nearly twice as that giving the higher one.

The corresponding plots for solutions containing *t*-BuOH deviate slightly from the straight line (Fig. 2), indicating that *t*-butyl alcohol radical interacts with HgBr. In reference to the results for HgCN,[4)] it is expected that the other alcohol radicals also react with HgBr. In the present system, however, the deviation from linearity in the decay kinetics may be negligible, because the attainable radical concentration is kept low owing to Reaction 7.

The residual absorbing species at shorter wavelengths may be ascribed to be Hg_2Br_2 in view of the similarity with the $HgCl_2$ system (Fig. 1).[1)] It may be supported by the fact that the slow increase of the absorption at 260 nm occurs simultaneously with the second order decay of HgBr (Fig. 3).

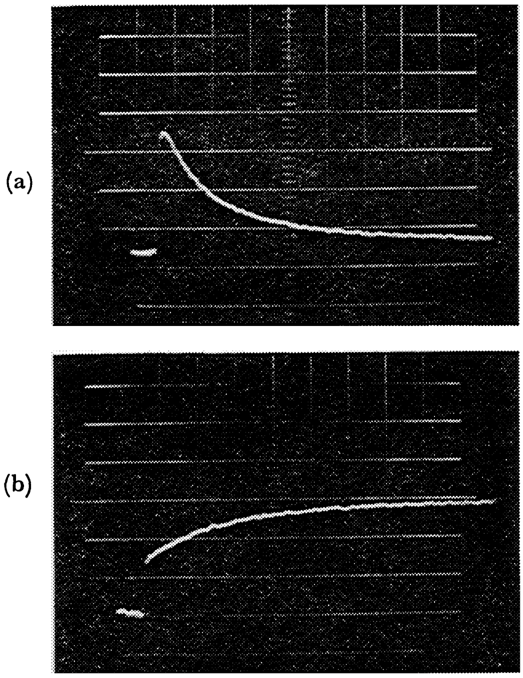

Fig. 3. Oscillographic traces obtained in a deaerated aqueous solution of 500 μM $HgBr_2$ and 10 mM *i*-Pr-OH: (a) 350 nm, (b) 260 nm; average dose, 2100 rad; ordinates, 4.5%/div., abscissa, 10 μs/div.

Figure 4 shows the absorption spectra obtained in a N_2O-saturated solution of $HgBr_2$. Two kinds of species are recognized: one absorbing at shorter wavelengths appears just after the pulse and disappears rapidly, while the other with an absorption maximum at 355 nm builds up slowly and decays according to a second order kinetics. The formation rate of the latter becomes greater with increasing $HgBr_2$ concentration. No residual absorption was found in this system.

In N_2O-saturated aqueous solutions the OH radical should work mainly as reactive species to solutes with

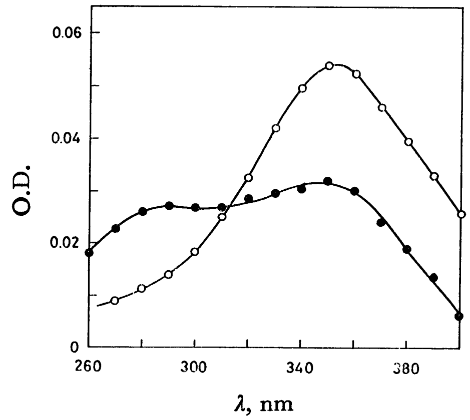

Fig. 4. Absorption spectra obtained in a N_2O-saturated aqueous solution of 500 μM $HgBr_2$, immediately (●) and 7 μs (○) after the pulse; average dose, 1600 rad.

$G(OH) = G_{e_{aq}^-} + G_{OH} = 5.5$.[10] Most of the former absorption, however, may be due to HgCl reduced by the H radical and some part of the e_{aq}^- in view of the results obtained in deaerated solutions. Though the absorption quantity at 280 nm seemed somewhat larger (initially about twice as much) than that in the solution containing *t*-BuOH as an OH scavenger, no evidence was obtained suggesting a species other than HgCl. The latter absorption would be interpreted by the occurrence of the oxidation of Br^-, since no evidence that mercury(II) ions in some other complexes are further oxidized by the OH radical.[2-4]

Radiolysis of aqueous solutions of KBr gives rise to transient Br_2^- ions having an absorption spectrum with a maximum at 360 nm ($\varepsilon^{360}=8200\ M^{-1}\ cm^{-1}$),[12] which is similar to the one at 7 μs after the pulse (Fig. 4).

$$Br^- + OH \longrightarrow Br + OH^- \qquad (8)$$

$$Br + Br^- \longrightarrow Br_2^- \qquad (9)$$

Contribution of the free Br^- to Br_2^- formation, however, should be ruled out, because $HgBr_2$ is little dissociable and little hydrolyzed in aqueous solutions.[13] Thus, the following processes might take place.

$$HgBr_2 + OH \longrightarrow HgBrOH + Br \qquad (10)$$

$$Br + HgBr_2 \xrightarrow{H_2O} HgBrOH + Br_2^- + H^+ \qquad (11)$$

If these processes actually occur, Br_2^- should recombine to produce the stable Br_3^- having an intense absorption with a peak at 267 nm ($\varepsilon \approx 40000\ M^{-1}\ cm^{-1}$)[14]

$$2Br_2^- \longrightarrow Br_3^- + Br^- \qquad (12)$$

It was found, however, that even in the case of a N_2O-KBr system such an intense absorption was observed only in the acidic solutions (pH 2). No residual absorption was observed in N_2O-saturated $HgBr_2$ solutions at the same pH. The results suggest that the 355 nm-transient species is not Br_2^- (Fig. 4). This may be supported by some characteristic differences between the transient and Br_2^-:

(i) ε^{360} of the transient obtained in N_2O-saturated $HgBr_2$ solutions (100—500 μM) is *ca.* 75% of that of Br_2^- appearing in a N_2O-saturated 1 mM KBr solution. Both values were compared with each other at very low doses (30—150 rad), to avoid the effect of decay (Fig. 5).

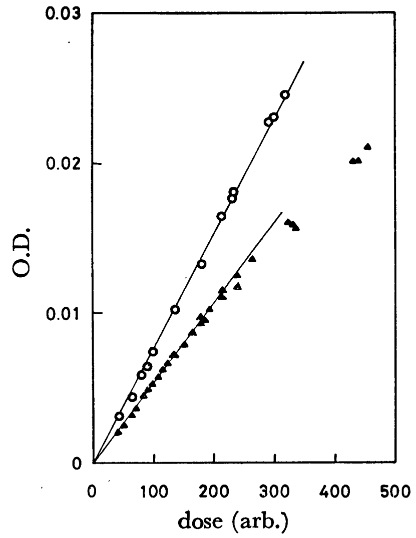

Fig. 5. Comparison between the 355 nm-absorption yields from Br_2^- in a N_2O-saturated KBr solution and the transient in a N_2O-saturated $HgBr_2$ solution: ○: N_2O+1 mM KBr, ▲: N_2O+500 μM $HgBr_2$. The dose unit is roughly in agreement with "rad", though not calibrated.

(ii) $2k/\varepsilon^{360}$ of the transient calculated from the slope of the plots of $1/D$ *vs.* t is about twice as much as that of Br_2^- (6.0 and $3.4\times10^5\ cm\ s^{-1}$, respectively, where the latter value is consistent with the reported one[15]).

Čerček pointed out the existence of the Br_3^{2-} ion in aqueous solutions of highly concentrated KBr.[16] It can be assumed that the transient can be a complex molecule such as $HgBr_3$ in view of the charge equivalency.

$$Br + HgBr_2 \longrightarrow HgBr_3 \qquad (13)$$

If the assumption is correct, Hg(II) seems to increase the stability of Br_3^{2-} structure since there exist few free Cl^- ions in the solution. Since the transient gives rise to no Br_3^- absorption after the second order decay, the bimolecular reaction of $HgBr_3$ would produce Br_2, though the determination of Br_2 was not carried out.

$$2HgBr_3 \longrightarrow 2HgBr_2 + Br_2 \qquad (14)$$

The second order rate constant of the transient formation was determined to be $9\times10^8\ M^{-1}\ s^{-1}$ from the analysis of the formation curve in N_2O-saturated solutions of 100—200 μM $HgBr_2$.

References

1) N. B. Nazhat and K. -D. Asmus, *J. Phys. Chem.*, **77**, 614 (1973).

2) S. Fujita, H. Horii, and S. Taniguchi, *J. Phys. Chem.*, **77**, 2868 (1973).

3) S. Fujita, H. Horii, T. Mori, and S. Taniguchi, *J. Phys. Chem.*, **79**, 960 (1975).

4) S. Fujita, H. Horii, T. Mori, and S. Taniguchi, *Bull. Chem. Soc. Jpn.*, **48**, 3067 (1975).

5) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isot.*, **18**, 493 (1967).

6) J. H. Bexendale *et al.*, *Nature (London)*, **201**, 468 (1964).

7) L. M. Dorfman and I. A. Taub, *J. Am. Chem. Soc.*, **85**, 2370 (1963); S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *ibid.*, **85**, 1375 (1963).

8) E. J. Hart, J. K. Thomas, and S. Gordon, *Rad. Res. Suppl.* **4**, 74 (1964).

9) G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael, "Pulse Radiolysis," ed. by M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Academic Press, London, (1965), p. 131.

10) G represents the number of species per 100 eV absorbed energy. Primary reactive species are produced with $G(e_{aq}^-)=2.7$, $G(OH)=2.8$, and $G(H)=0.6$, respectively.[11]

11) M. S. Matheson and L. M. Dorfman, "Pulsed Radiolysis," The M. I. T. Press, Cambridge, Mass. (1969).

12) H. C. Sutton, G. E. Adams, J. W. Boag, and B. D. Michael, "Pulse Radiolysis," ed. by M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Academic Press, London (1965), p 61.

13) B. J. Aylet, "Comprehensive Inorganic Chemistry," Vol. 3, ed. by J. C. Bailar, H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, Pergamon Press, Oxford (1973), p. 296.

14) A. Rafi and H. C. Sutton, *Trans. Faraday Soc.*, **61**, 877 (1965).

15) M. S. Matheson, W. A. Mulac, J. L. Weeks, and J. Rabani, *J. Phys. Chem.*, **70**, 2092 (1966).

16) B. Čerček, *Int. J. Radiat. Phys. Chem.*, **4**, 25 (1972).