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The one electron reduction of Hg^{2+} by 1-hydroxyalkyl radicals in aqueous solution: a pulse radiolysis study

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Abstract

The rate constants for the reduction of the divalent mercury ion Hg^{2+} by alcohol radicals, which are produced in acidic aqueous solutions containing methanol, ethanol or 2-propanol, are determined by optical absorption measurements to be 7.0×10^8 , 3.8×10^8 or $3.1 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively.

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Keywords: Divalent mercury ion; 1-hydroxyalkyl radicals; One electron reduction; Rate constant; Pulse radiolysis

1. Introduction

In pulse radiolysis, the reduction of Hg(II) ions and HgX_2 compounds, where X stands for Cl, Br, I, CNS or SCN, by hydrated electrons or hydrogen atoms results in Hg(I) species which are unstable in aqueous solution (Ershov, 1997). In acidic aqueous solutions, the reduction of divalent mercury by hydrogen atoms yields intermediate Hg^+ ions, which exhibit an absorption with two bands at 225 and 255 nm (Fujita et al., 1973, 1975). In the present paper, we demonstrate that in acidic aqueous solution Hg^{2+} ions can also be reduced to Hg^+ by 1-hydroxyalkyl radicals, i.e., radicals produced from methanol, ethanol or 2-propanol.

2. Experimental

The pulse radiolysis apparatus (Janata, 1992) and the computer software (Janata, 1994) of the 4 MeV van de Graaff accelerator facility ELBENA at the Hahn-Meitner-Institut were described previously. The duration

of the electron pulses was set to 20 ns (Janata and Gutsch, 1998). The optical signals were derived from the average of 10 individual experiments. The optical absorption was calculated by dividing the optical density by the concentration of the radicals (c) generated in a pulse and by the length of the optical cell ($l = 1.5 \text{ cm}$), and thus is expressed in units of ϵ . The absorbed dose per pulse was calibrated by using $\epsilon = 1.9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for the e_{aq}^- absorption at 700 nm (Hug, 1981). The yield of electrons in neutral water was taken to be 2.6 species per 100 eV of absorbed energy (Buxton et al., 1988). The solutions were prepared daily using triply distilled water and were deaerated with argon. The software for the simulation of kinetic data was described elsewhere (Janata, 2003a, b). High transmission band-pass filters (UV-R types, Schott) were inserted in front of the monochromator in order to avoid stray-light effects.

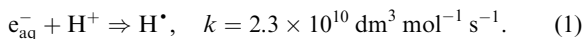
3. Results and discussion

Acidic solutions of mercury perchlorate also containing methanol, ethanol or 2-propanol at pH 1.5 were studied. The solutions were purged with argon. In these solutions, hydrated electrons formed during the

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radiolysis of water are converted into hydrogen atoms according to



The alcohol concentrations were high enough to ensure that all hydrogen atoms and hydroxyl radicals react with the alcohol (RH) according to



and



where R^\bullet is $^\bullet CH_2OH$, $CH_3^\bullet CHOH$ or $(CH_3)_2^\bullet COH$, and $k_2 = 1.1 \times 10^6$, 1.8×10^7 or $5.3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $k_3 = 9.0 \times 10^8$, 2.2×10^9 or $2.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, for methanol, ethanol or 2-propanol, respectively (Alam et al., 2001; Janata, 2003a,b). The alcohol radical

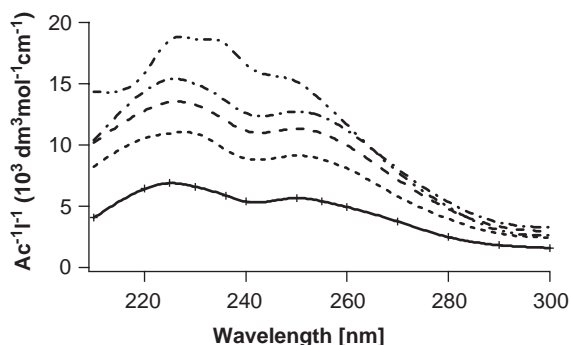


Fig. 1. Difference spectra at various times after irradiation of a solution containing $1 \times 10^{-3} \text{ mol dm}^{-3} \text{ Hg}(\text{ClO}_4)_2$, $2 \text{ mol dm}^{-3} \text{ MeOH}$, at pH 1.5 and purged with Ar. Time after irradiation: 0.5 μs (solid), 1 μs (dots), 1.5 μs (dashes), 2 μs (dot and dashes) and 20 μs (double dots and dashes). Pulse duration is 20 ns; dose per pulse corresponds to $1.7 \times 10^{-6} \text{ mol dm}^{-3}$ of alcohol radicals with $G(e_{aq}^- + OH + H) = 2.6 + 2.7 + 0.6 = 5.3$.

subsequently reacts with the divalent mercury ion via

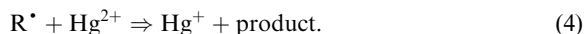
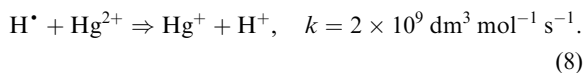
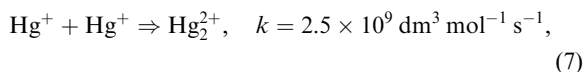


Fig. 1 shows the spectra obtained for a solution containing methanol at various times after the impingement of the irradiating pulse. An absorption consisting of two bands at 225 and 255 nm can clearly be observed at times of up to 2 μs , while at longer times a broad absorption at around 230 nm dominates. The absorption at shorter times has been assigned to Hg^+ (Fujita et al., 1973), while the band at around 230 nm belongs to Hg_2^{2+} , which is formed as a result of Hg^+ recombination (Fujita et al., 1973). Basically, the same spectrum was also obtained at 20 μs for solutions containing ethanol or 2-propanol. Fig. 2 shows the build-up of Hg^+ for all three alcohols at 290 nm where there is little interference with the formation of Hg_2^{2+} .

The transient absorption curves in Fig. 2 were analyzed using computer simulation for a reaction mechanism consisting of reactions (1)–(4) and the following ones as well:



The reactions are included in the simulation with known rate constants for reactions (6) and (8) (Buxton et al., 1988) and for reaction (7) (Pikaev et al., 1975; Buxton et al., 1995). The rate constants for the recombination of the alcohol radicals are: $k_5 = 2.4 \times 10^9$, 1.5×10^9 , and $1.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for methanol, ethanol, and 2-propanol, respectively (Alam et al.,

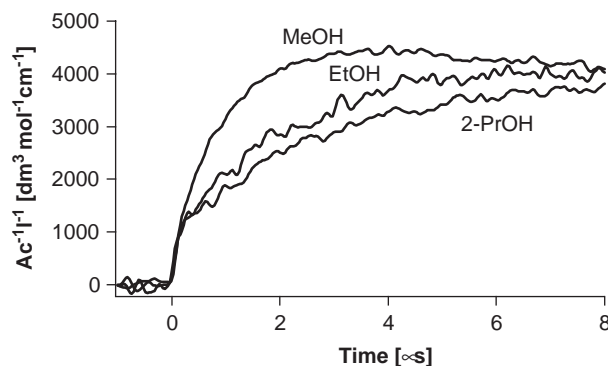


Fig. 2. Kinetic curves of the Hg^+ build-up at 290 nm for solutions of $1 \times 10^{-3} \text{ mol dm}^{-3} \text{ Hg}(\text{ClO}_4)_2$, Ar, pH 1.5 and $2 \text{ mol dm}^{-3} \text{ MeOH}$, $2 \text{ mol dm}^{-3} \text{ EtOH}$ and $2 \text{ mol dm}^{-3} \text{ 2-PrOH}$. 20 ns pulses with a dose corresponding to $1.8 \times 10^{-6} \text{ mol dm}^{-3}$ of alcohol radicals.

2001). For acidic aqueous solutions of these alcohols, computer simulation reveals the following values for the rate constant of reaction (4): 7.0×10^8 , 3.8×10^8 and $3.1 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively.

These values are lower than expected for diffusion controlled reactions. Moreover, the values of the rate constants decrease for methanol, ethanol and 2-propanol in that order while their reduction potentials increase correspondingly, i.e., -1.18 V for methanol, -1.25 V for ethanol and -1.39 V for 2-propanol (Wardman, 1989). A short-lived intermediate complex of an mercury ion and of an alcohol radical might be formed initially, after which electron transfer and separation could occur resulting in reduced mercury ions and products. Because steric hindrance, which depends on the size of the alcohol radical, would affect the rate of formation of the intermediate complex, the formation of this complex could be the rate determining step.

4. Conclusions

It has been shown that, in addition to hydrated electrons and hydrogen atoms, 1-hydroxyalkyl radicals, as derived from methanol, ethanol, or 2-propanol, also have the power to reduce divalent mercuric ions in acidic aqueous solutions.

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References

- Alam, M.S., Rao, B.S.M., Janata, E., 2001. A pulse radiolysis study of H atom reactions with aliphatic alcohols: evaluation of kinetics by direct optical absorption measurement. *Phys. Chem. Chem. Phys.* 3, 2622–2624.
- Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\bullet}\text{OH}/^{\bullet}\text{O}^{\bullet}$) in aqueous solution. *J. Phys. Chem. Rev. Data* 17, 513–886.
- Buxton, G.V., Mulazzani, Q.G., Ross, A.B., 1995. Critical review of rate constants for reactions of transients from metal ions and metal complexes in aqueous solution. *J. Phys. Chem. Rev. Data* 24, 1055–1349.
- Ershov, B.G., 1997. Metal ions in unusual and unstable oxidation states in aqueous solutions; preparation and properties. *Russ. Chem. Rev.* 66, 93–105.
- Fujita, S., Horii, H., Taniguchi, S., 1973. Pulse radiolysis of mercuric ion in aqueous solutions. *J. Phys. Chem.* 77, 2868–2871.
- Fujita, S., Horii, H., Mori, T., Taniguchi, S., 1975. Pulse radiolysis of mercuric oxide in neutral aqueous solutions. *J. Phys. Chem.* 79, 960–964.
- Hug, G.L., 1981. Optical spectra of nonmetallic inorganic transient species in aqueous solution, NSRDS-NBS 69.
- Janata, E., 1992. Instrumentation of kinetic spectroscopy-10. A modular data acquisition system for laser flash photolysis and pulse radiolysis experiments. *Radiat. Phys. Chem.* 40, 437–443.
- Janata, E., 1994. Instrumentation of kinetic spectroscopy-12. Software for data acquisition in kinetic experiments. *Radiat. Phys. Chem.* 48, 449–454.
- Janata, E., 2002. Direct optical observation of the formation of some aliphatic alcohol radicals. A pulse radiolysis study. *Proc. Indian Acad. Sci. (Chem. Sci.)* 114, 731–737.
- Janata, E., 2003a. Instrumentation of kinetic spectroscopy. A method for the simulation of kinetics of reaction mechanisms. *Radiat. Phys. Chem.* 66, 219–222.
- Janata, E., Gutsch, W., 1998. Instrumentation of kinetic spectroscopy-15. Injector pulse generators for electron accelerators, Part 3. *Radiat. Phys. Chem.* 51, 65.
- Pikaev, A.K., Sibirskaya, G.K., Spitsyn, V.I., 1975. Pulsed radiolysis of aqueous solutions of compounds of divalent mercury. *Dokl. Phys. Chem.* 224, 994–997.
- Wardman, P., 1989. Reduction potentials of one-electron couples involving free radicals in aqueous solution. *J. Phys. Chem. Ref. Data* 18 (4), 1637–1755.