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Reactivity of 1-hydroxyalkyl radicals in the reduction of Hg^{2+} and I_2 in aqueous solutions

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The kinetics and mechanism of reduction of Hg^{2+} ions and I_2 molecules with $^{\cdot}CH_2OH$, $Me^{\cdot}CHOH$ and $Me_2^{\cdot}COH$ radicals were proposed based on a pulse radiolysis study.

The reactivity of organic radicals in the one-electron reduction of organic and inorganic compounds in aqueous solutions essentially depends on the reaction mechanism and the rate-limiting step.[1] In this work, we measured the reaction rate constants of the reduction of Hg^{2+} ions and I_2 molecules with $H^{\cdot}$ atoms and the 1-hydroxyalkyl radicals $^{\cdot}CH_2OH$, $Me^{\cdot}CHOH$ and $Me_2^{\cdot}COH$, which are significantly different in size and reduction potentials.[2] The Hg^{2+} ions and I_2 molecules were chosen as test species because their structures in aqueous alcohol solutions are dramatically different (Hg^{2+} ions have a hydration sphere, whereas I_2 molecules most likely form charge-transfer complexes with water and alcohol molecules[3]), and this circumstance can affect the mechanism of one-electron reduction.

The pulse radiolysis unit based on a van de Graaff generator with an energy of 3.8 MeV and the computer software were described elsewhere.[4–6] An optical signal was obtained by averaging 10 individual experiments. The optical absorption was calculated by dividing the absorbance (A) by the optical path length (l = 1.5 cm). The absorbed dose was calculated from the known $\varepsilon = 1.9\times10^4$ dm^3 mol^{-1} cm^{-1} for hydrated electrons e^-_{aq} at 700 nm.[7] The yield of e^-_{aq} in water at pH 7 was taken equal to 2.6 particle/100 eV (0.269 μmol J^{-1}).[8] Other experimental conditions were described in detail elsewhere.[9]

We studied acidic aqueous solutions (pH 1–2, $HClO_4$) of $Hg(ClO_4)_2$ (2×10^{-4}–2×10^{-3} M) and I_2 (2×10^{-5}–2×10^{-4} M) containing an alcohol (methanol, ethanol or isopropanol). The solutions were saturated with argon. In these solutions, e^-_{aq} are converted into H atoms in the reaction

$$e^-_{aq} + H^+ \rightarrow H^{\cdot} \quad k = 2.3\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ \text{(ref. 8)}. \qquad (1)$$

The concentrations of the alcohols were sufficiently high (up to 2 M) to provide almost complete scavenging of H and OH by the alcohols (RH) according to the following reactions:

$$H^{\cdot} + RH \rightarrow R^{\cdot} + H_2, \qquad (2)$$

$$^{\cdot}OH + RH \rightarrow R^{\cdot} + H_2O, \qquad (3)$$

where $R^{\cdot}$ is the alcohol radical $^{\cdot}CH_2OH$, $Me^{\cdot}CHOH$ or $Me_2^{\cdot}COH$; $k_2 = 1.1\times10^6$, 1.8×10^7 or 5.3×10^7 dm^3 mol^{-1} s^{-1}; and $k_3 = 9.0\times10^8$, 2.2×10^9 or 2.0×10^9 dm^3 mol^{-1} s^{-1} for MeOH, $MeCH_2OH$ or Me_2CHOH, respectively.[10] We found by calculations that, under the specified experimental conditions (high concentrations of alcohols), the predominant portions of $H^{\cdot}$ and $^{\cdot}OH$, as a rule, were converted into alcohol radicals. Their participation in other reactions was taken into consideration in the determination of rate constants.

Next, the alcohol radicals reacted with the Hg^{2+} ion or the I_2 molecule in the reactions

$$R^{\cdot} + Hg^{2+} \rightarrow Hg^+ + X + H^+, \qquad (4)$$

$$R^{\cdot} + I_2 \rightarrow I_2^{\cdot-} + X + H^+, \qquad (5)$$

where X is CH_2O, MeCHO or Me_2CO for MeOH, $MeCH_2OH$ or Me_2CHOH solutions, respectively.

The transient optical spectra of irradiated $Hg(ClO_4)_2$ solutions exhibited two bands with maxima at 225 and 255 nm 2 μs after the action of an electron pulse; these bands were attributed to the Hg^+ ion.[11,12] According to our data, the molar absorption coefficient of Hg^+ at 255 nm is $(1.7\pm0.1)\times10^4$ dm^3 mol^{-1} cm^{-1}. It is higher than $(1.4\pm0.1)\times10^4$ dm^3 mol^{-1} cm^{-1} obtained by Fujita *et al.*[9] At times longer than 8 μs, a band with a maximum at 230 nm due to the Hg_2^{2+} ion was predominant in the spectrum.[11,12] This ion resulted from the recombination of Hg^+. Figure 1(*a*) illustrates the kinetics of Hg^+ formation in a 1×10^{-3} M $Hg(ClO_4)_2$ solution for all the alcohols tested (2 M) at a wavelength of 290 nm, at which the contribution of Hg_2^{2+} absorption was minimum. The increase of Hg^+ absorbance is slower in the order methanol > ethanol > isopropanol; however, the absorbance at 8 μs is the same and corresponds to the molar absorption coefficient $\varepsilon_{290}(Hg^+) = 4.0\times10^3$ dm^3 mol^{-1} cm^{-1}. Thus, Hg^+ was formed in the same yield in all the cases, and it corresponds to $c = ([e^-_{aq}] + [H^{\cdot}] + [^{\cdot}OH])$ according to reactions (1)–(4).

Figure 1(*b*) illustrates the increase in the absorbance at 725 nm in I_2 solutions containing 1×10^{-3} M or 0.2 M MeCHOH (curves *2* and *3*, respectively) or 2.4 M MeOH (curve *3*) after the action of an electron pulse. The kinetics of the build-up of a signal at 725 nm was also studied with the use of $MeCH_2OH$. The rapid appearance and disappearance of the absorbance immediately after the end of the electron pulse resulted from the increase in the absorbance due to the formation and decay of e^-_{aq}. The subsequent increase in the absorption was due to the formation of $I_2^{\cdot-}$.[7] At first glance, it seems surprising that the lower the concentration of Me_2CHOH in solution, the more rapid the absorbance build-up [*cf.* curves *1* and *2* in Figure 1(*b*)]. This is due to competition between the alcohol [reaction (2)] and iodine for H atoms:

$$H^{\cdot} + I_2 \rightarrow I_2^{\cdot-} + H^+. \quad k = 3.5\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ \text{(ref. 8)}. \qquad (6)$$

In turn, alcohol radicals formed by reaction (2) also reduced I_2 [reaction (4)]. It is likely that reaction (6) is more rapid than reaction (5).

Data on the formation of Hg^+ [Figure 1(*a*)] were analysed based on reactions (1)–(4) and the following reactions:

$$R^{\cdot} + R^{\cdot} \rightarrow \text{product} \qquad (7)$$

$$H^{\cdot} + H^{\cdot} \rightarrow H_2 \quad k = 1\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ \text{(ref. 8)} \qquad (8)$$

$$Hg^+ + Hg^+ \rightarrow Hg_2^{2+} \quad k = 2.5\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ \text{(ref. 13)} \qquad (9)$$

$$H^{\cdot} + Hg^{2+} \rightarrow Hg^+ + H^+ \quad k = 2\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ \text{(ref. 8)} \qquad (10)$$

The rate constants of recombination of the alcohol radicals[10] were equal to $k_7 = 2.4\times10^9$, 1.5×10^9 and 1.1×10^9 dm^3 mol^{-1} s^{-1} for $^{\cdot}CH_2OH$, $Me^{\cdot}CHOH$ and $Me_2^{\cdot}COH$, respectively. The total yield of e^-_{aq}, $H^{\cdot}$ atoms and $^{\cdot}OH$ radicals in water was taken equal to $G(e^-_{aq} + H^{\cdot} + {}^{\cdot}OH) = 2.6 + 2.7 + 0.6 = 5.9$. A computer simulation resulted in the following rate constants of reaction (4): 7.0×10^8, 3.8×10^8 and 3.1×10^8 dm^3 mol^{-1} s^{-1} for $^{\cdot}CH_2OH$, $Me^{\cdot}CHOH$ and $Me_2^{\cdot}COH$, respectively. The resulting constants are much lower than the values expected for diffusion-controlled reactions. Thus, the value of k_4 decreases in the order $^{\cdot}CH_2OH$, $Me^{\cdot}CHOH$ and $Me_2^{\cdot}COH$.

We used an analogous approach to calculate the rate constants of reactions (5) between alcohol radicals and I_2 from kinetic data on the appearance of absorbance at 725 nm due to $I_2^{\cdot-}$ [Figure 1(*b*)]. For this purpose, along with reactions (1)–(3) and

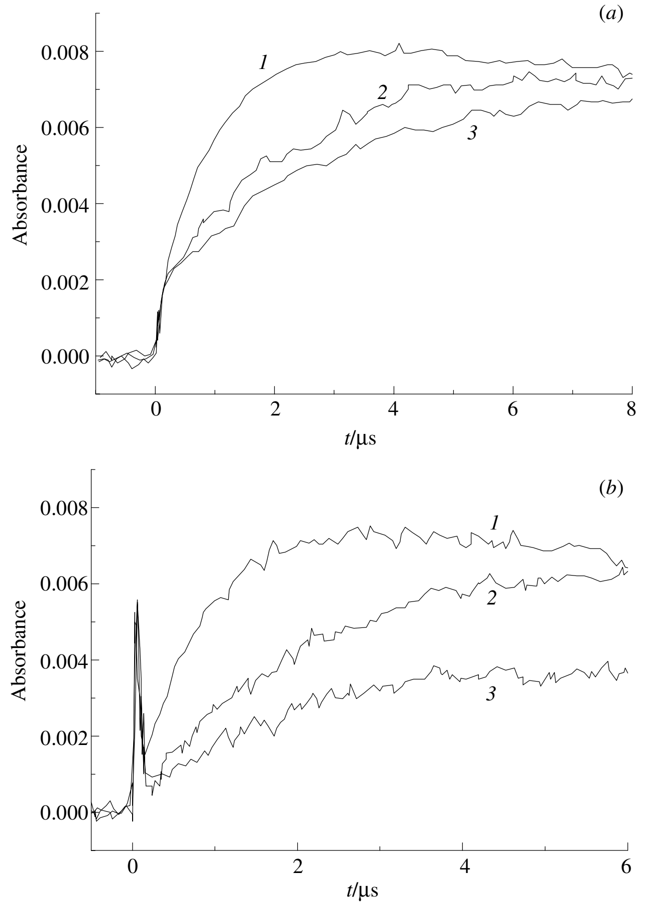

Figure 1 (*a*) Kinetic curves of the absorbance of Hg^+ at 290 nm for a 1×10^{-3} M $Hg(ClO_4)_2$ solution (Ar, pH 1.5) containing (*1*) 2 M MeOH, (*2*) 2 M $MeCH_2OH$ or (*3*) 2 M Me_2CHOH. 20 ns pulse; absorbed dose of 2.0×10^{16} eV ml^{-1}. (*b*) Kinetic curves of the absorption of $I_2^{\cdot-}$ at 725 nm for a 5×10^{-5} M I_2 solution (Ar, pH 2) containing (*1*) 1×10^{-3} M, (*2*) 0.2 M Me_2CHOH or (*3*) 2.4 M MeOH. 20 ns pulse; absorbed dose of 2.7×10^{16} eV ml^{-1}.

(5)–(8), the following reactions were also taken into account:

$I_2^{\cdot-} + I_2^{\cdot-} \rightarrow I_3^- + I^-$ $\quad 2k = 4.6\times10^9$ dm^3 mol^{-1} s^{-1} (11)
$I^{\cdot} + I^- \Leftrightarrow I_2^{\cdot-}$ $\quad k_f = 8.8\times10^9$ dm^3 mol^{-1} s^{-1} (12)
$\quad k_b = 7\times10^4$ s^{-1}
$I_2 + I^- \Leftrightarrow I_3^-$ $\quad k_f = 5.6\times10^9$ dm^3 mol^{-1} s^{-1} (13)
$\quad k_b = 7.5\times10^6$ s^{-1}
$I^{\cdot} + I^{\cdot} \rightarrow I_2$ $\quad 2k = 3\times10^{10}$ dm^3 mol^{-1} s^{-1} (14)

Here, k_f and k_b are the rate constants of forward and reverse reactions, respectively. All the rate constants (except for k_5) and ε values for the reactants and products are known.[14,15] The values of k_5 for $^{\cdot}CH_2OH$, $Me^{\cdot}CHOH$ and $Me_2^{\cdot}COH$ were found to be equal to 5.0×10^9, 6.5×10^9, and 8.0×10^9 dm^3 mol^{-1} s^{-1}, respectively. Thus, in contrast to reactions with Hg^{2+}, the reaction rate constants of alcohol radicals with I_2 increase in the above order. Note that the increase in the rate constants in the order of increasing size of the radical unambiguously indicates that the reactions with the participation of the radicals are not diffusion controlled.

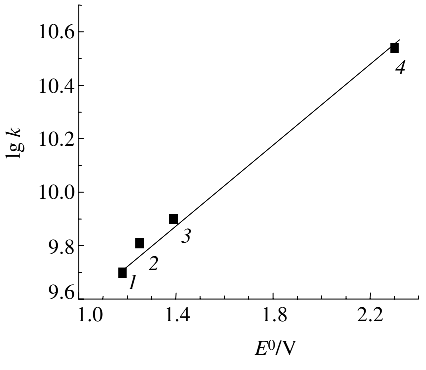

Figure 2 Dependence of the reaction rate constants of (*1*) $^{\cdot}CH_2OH$, (*2*) $Me^{\cdot}CHOH$ or (*3*) $Me_2^{\cdot}COH$ radicals and (*4*) H atoms[6] with I_2 on the reduction potential. Ordinate: log $k(I_2 + R^{\cdot})$. Abscissa: $E^\circ(R^{\cdot})$/V.

Table 1 Redox potentials[3] and reaction rate constants of H atoms[6] and alcohol radicals with Hg^{2+} and I_2.[a]

Radical	E^0/V	k/dm^3 mol^{-1} s^{-1}	
		Hg^{2+}	I_2
$H^{\cdot}$	–2.30	2.0×10^9	3.5×10^{10}
$^{\cdot}CH_2OH$	–1.18	7.0×10^8	5.0×10^9
$Me^{\cdot}CHOH$	–1.25	3.8×10^8	6.5×10^9
$Me_2^{\cdot}COH$	–1.39	3.1×10^8	8.0×10^9

[a] The uncertainty in the rate constants is no higher than ±15%.

The higher the reduction potentials, the higher the rate constants of reactions of alcohol radicals, as well as $H^{\cdot}$ atoms, with I_2 (see Table 1). Moreover, log k_5 is a linear function of the reduction potential of the reactant. Therefore, we can conclude that the reducing power is responsible for the efficiency of outer-sphere electron transfer from the $H^{\cdot}$ atom and an alcohol radical to the I_2 molecule.

The reaction rate constants (k_4) of the Hg^{2+} ion with $H^{\cdot}$ atoms and alcohol radicals increased with decreasing size of the reducing agent (Table 1). Thus, it is believed that the interaction of $R^{\cdot}$ with Hg^{2+} resulted in the short-lived complex $[Hg^{2+}\cdots R^{\cdot}]$. Next, outer-sphere electron transfer and the separation of reaction products occurred. Note that the formation of stable complexes in analogous reactions is typical of many metals, especially, transition metals.[16] Because of steric hindrances (the greater the size of the radical, the more significant steric hindrances), the rate of formation of an intermediate complex limits the rate of the reduction process, as it was observed experimentally.

Thus, we can conclude that, at least for some reduction reactions with the participation of organic radicals, a redox process is developed in accordance with a classical scheme, which corresponds to reactions in the outer sphere and in the inner sphere. For the former type, the interaction of an oxidising agent with a reducing agent is insignificant in the course of electron transfer, and it most likely does not affect the coordination spheres. As can be seen, these reactions exhibit the dependence of the reactivity of organic radicals on the reduction potential. For reactions of the latter type, a necessary condition is the occurrence of a strong bond between the oxidising agent and the reducing agent in the course of electron transfer. This results from the formation of an intermediate complex. In this case, the rate of electron transfer is limited by the above step and essentially depends on the steric factor.

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