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The Use of Conjugated Scavengers to Determine the Rate Constants of Fast Reactions in Aqueous Solutions by Pulse Radiolysis

Andrei V. Gogolev, Vladimir P. Shilov, Alexandr M. Fedoseev and Alexei K. Pikaev*
Institute of Physical Chemistry, Russian Academy of Sciences, 117915 Moscow, Russian Federation.
Fax: +7 095 952 7514

It has been shown that pairs of conjugated scavengers can be used for the determination of rate constants of fast reactions in aqueous solutions by pulse radiolysis; the rate constants of reactions of U^{V} and Cu^{I} with Ce^{IV} and SO_4^- and U^{V} with $HSeO_3$ have been measured.

Pulse radiolysis is widely used for the solution of various problems in physical, inorganic and organic chemistry and biochemistry.[1,2] One of the most important trends is the determination of the rate constants of fast reactions in solution. A spectrophotometric identification of the short-lived species formed upon the action of an electron pulse is used to measure the decay and formation kinetics of the optical absorption of reacting species and reaction products. However, the instability of the reagents (*e.g.*, due to their mutual interaction) sometimes does not allow solutions containing them to be used. In such cases, the conjugated radical scavengers (*i.e.* two substances, one of which reacts rapidly with OH radicals and the second one with hydrated electrons, e_{aq}^-, and hydrogen atoms) may be utilized; the primary radiolysis products react with the conjugated scavengers to form the reactant species. The present communication illustrates this possibility using as examples the reactions: $Ce^{IV}+Cu^{I}$, $U^{V}+Ce^{IV}$, $Cu^{I}+SO_4^-$, $U^{V}+SO_4^-$ and $U^{V}+HSeO_3$.

A pulse radiolysis facility with spectrophotometric identification of transient species within the range 240–1100 nm was used. The facility operates on the basis of an U–12 electron accelerator (pulse duration 2.3 μs, electron energy 5 MeV). Doses per pulse determined by the rhodanide method[3] were 5–20 Gy. The salts $Ce_2(SO_4)_3 \cdot nH_2O$, $CuSO_4 \cdot 5H_2O$ and $UO_2SO_4 \cdot nH_2O$ were additionally purified by recrystallization from an aqueous solution. Twice-distilled water and sulfuric and perchloric acids of chemically-pure grade were used to prepare the solutions. High-purity argon was bubbled through the solutions to remove air.

It is well-known (see, *e.g.*, ref. 1) that the action of ionizing radiation on water leads to the formation of radical and molecular products, reaction (1).

$$H_2O \rightarrow H, OH, e_{aq}^-, H_2, H_2O_2, H^+ \qquad (1)$$

In a sufficiently acid solution, e_{aq}^- is converted rapidly to the H atom, eqn. (2),

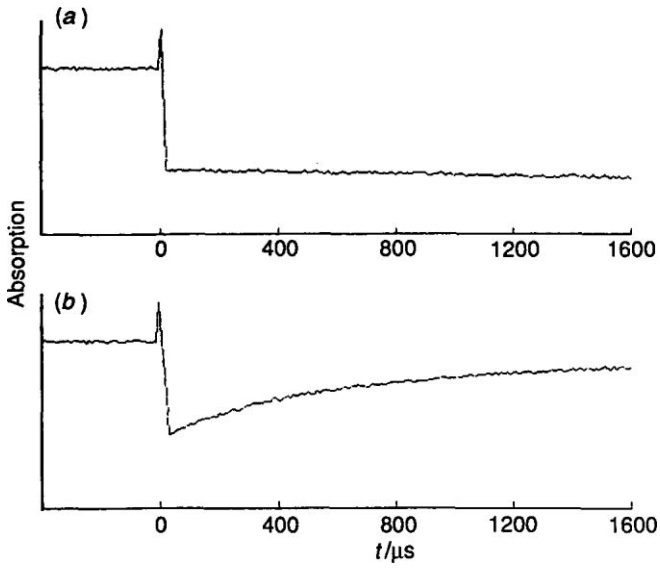

Fig.1 Transient optical absorption at 360 nm after the pulse (dose 15 Gy) in a solution containing 0.03 M $Ce_2(SO_4)_3$ and 0.1M H_2SO_4 (*a*) without Cu^{II} ions and (*b*) with 0.1M $CuSO_4$

$$e_{aq}^- + H^+ \rightarrow H \quad k_2 = (1-2) \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}\ ^4 \quad (2)$$

and after the pulse the solution contains H and OH radicals and also molecular products. The reactions of H_2O_2 are relatively slow[5] and do not occur within the time range considered. Molecular hydrogen also does not take part in the fast processes.

$$Cu^{II} + H \rightarrow H^+ + Cu^I \quad k_3 = 6.3 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}\ ^4 \quad (3)$$

$$Ce^{III} + OH \rightarrow Ce^{IV} + OH^- \quad k_4 = 3 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}\ ^4 \quad (4)$$

$$Cu^{II} + e_{aq}^- \rightarrow Cu^I \quad k_5 = 3.5 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}\ ^4 \quad (5)$$

Reactions (3)–(5) are completed in aqueous solutions containing 0.1M $CuSO_4$, 0.03M $Ce_2(SO_4)_3$ and 0.1M H_2SO_4 during the 2.3 μs pulse. The resulting cerium(IV) sulfate complexes show intense optical absorption with a maximum at 320 nm. The measurements were carried out at 360 nm (this was convenient under our experimental conditions), at which the absorption due to cerium(IV) sulfate complexes is rather intense. In the absence of Cu^{II} ions the optical absorption of Ce^{IV} after the pulse does not decrease within the time range of interest (see Fig. 1). In the presence of Cu^{II} ions, a decrease in the optical absorption (see Fig. 1) is observed, which is accounted for by reaction (6).

$$Cu^I + Ce^{IV} \rightarrow Cu^{II} + Ce^{III} \quad (6)$$

The yield of Cu^I ions is somewhat higher than that of Ce^{IV} ions; however, the greater part of the kinetic curve is consistent with a second-order reaction. The slope of the curve $1/D_{360}$ *vs.* t at an initial stage, where D_{360} is the optical absorption at 360 nm and t is the time after the pulse, is equal to $k_6/\varepsilon l$ (l is the optical path length and ε is the extinction coefficient of cerium (IV) at 360 nm; under our conditions it is equal to 2430 $dm^3\ mol^{-1}\ cm^{-1}$). The k_6 value calculated by this method is given in Table 1.

Computer simulation of the decay kinetics of optical absorption (numerical integration of the corresponding differential equations system using the Runge–Kutta method) with the above-mentioned inequality of the initial concentrations Ce^{IV} and Cu^I ($G[Ce^{IV}] = G_{OH} = 2.95$, $G[Cu^I] = G_H + G_{e_{aq}^-} = 3.65$) gives a k_6 value that agrees, within the calculation error, with that determined from the slope of the curve $1/D_{360}$ *vs.* t and is equal to $(7.0 \pm 1.0) \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$.

Table 1 Reaction rate constants determined using conjugated scavengers

No.	Reaction	Medium	k/$dm^3\ mol^{-1}\ s^{-1}$
6	$Cu^I + Ce^{IV}$	0.1M H_2SO_4	$(7.0 \pm 0.8) \times 10^8$
8	$U^V + Ce^{IV}$	0.1M H_2SO_4	$(2.0 \pm 0.3) \times 10^7$
9	$Cu^I + SO_4^-$	2.0M H_2SO_4	$(1.5 \pm 0.2) \times 10^{10}$
9	$Cu^I + SO_4^-$	1.1M H_2SO_4	$(1.8 \pm 0.2) \times 10^{10}$
10	$U^V + SO_4^-$	1.5M H_2SO_4	$(7.7 \pm 0.9) \times 10^9$
11	$U^V + HSeO_3$	0.1M $HClO_4$	$(1.4 \pm 0.2) \times 10^{10}$
11	$U^V + HSeO_3$	0.9M $HClO_4$	$(1.8 \pm 0.3) \times 10^{10}$

Reactions (1), (2), (4) and reactions (7) and (8)

$$U^{VI} + H \rightarrow U^V + H^+ \quad k_7 = 4.5 \times 10^7\ dm^3\ mol^{-1}\ s^{1,6} \quad (7)$$

$$U^V + Ce^{IV} \rightarrow U^{VI} + Ce^{III} \quad (8)$$

take place in solutions containing 0.03 M $Ce_2(SO_4)_3$, 0.2M UO_2SO_4 and 0.1M H_2SO_4. The k_8 value, calculated in a similar manner as for k_6, is given in Table 1.

The rate constants of the reactions (9)–(11)

$$Cu^I + SO_4^- \rightarrow Cu^{II} + SO_4^{2-} \quad (9)$$

$$U^V + SO_4^- \rightarrow U^{VI} + SO_4^{2-} \quad (10)$$

$$U^V + HSeO_3 \rightarrow U^{VI} + HSeO_3^- \quad (11)$$

were determined by the same method. The radicals SO_4^- and $HSeO_3$ resulted from the reactions of HSO_4^-, H_2SO_4, $HSeO_3^-$ and H_2SeO_3 with OH radicals. The decrease in the optical absorption of SO_4^- at $\lambda = 450$ nm ($\varepsilon = 1050\ dm^3\ mol^{-1}\ cm^{-1}$ [1,1]) was measured to determine k_9 and k_{10}. For the determination of k_{11} the decay of the $HSeO_3$ optical density was monitored at 430 nm ($\varepsilon = 930\ dm^3\ mol^{-1}\ cm^{-1}$ [1,7]). The values of k_9, k_{10} and k_{11} are listed in Table 1.

It should be noted that the redox potentials of the pairs Cu^{II}/Cu^I and U^{VI}/U^V are equal to 0.16 V.[8] The difference in the k_6 and k_8 values seems to be due to a more stable hydrate sphere of the UO_2^+ ion and the presence of valent electrons on the inner f-orbitals of the ion.

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