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Kinetic Isotope Effect for γ-Radiolytic Reduction of Divalent Lead in Aqueous Solutions

Aleksandr Yu. Garnov, Sergey I. Nikitenko,* Arkadii A. Lukonin and Boris G. Ershov

Institute of Physical Chemistry, Russian Academy of Sciences, 117915 Moscow, Russian Federation. Fax: +7 095 335 1778

The kinetic isotope effect has been observed for γ-radiolytic reduction of Pb^{II} in aqueous formate solutions and the values of the isotope separation coefficient (α) for $^{208/207}Pb$, $^{208/206}Pb$ and $^{208/204}Pb$ have been determined.

Recently, kinetic isotope effects have been observed in Pu^{V} disproportionation reactions[1–3] and in the electrochemical reduction of Pu^{III}.[4] In the systems studied the reaction products were enriched with heavy plutonium isotopes. The value of the isotope separation coefficient (α) for $^{242}Pu/^{239}Pu$ was observed to be 1.025–1.052. It is therefore interesting to study the kinetic isotope effects in redox processes of other heavy elements.

It is known[5–7] that Pb^{II} ions in aqueous solution in the presence of organic reductants are reduced radiolytically to unstable Pb^{I} ions followed by reduction to metallic lead. It can be assumed that significant rearrangement of the reactant structure accompanied by phase transfer can lead, as in the systems with plutonium studied earlier, to a kinetic isotope effect.

A solution (deaerated by argon) of 0.01 mol dm^{-3} $Pb(ClO_4)_2$ containing 0.01–0.1 mol dm^{-3} HCOONa or 0.1 mol dm^{-3} $Pr^{i}OH$ was used for irradiation, which was performed by a ^{60}Co source. The power of the irradiation dose was 1.1 Mrad h^{-1}.

After irradiation the separated precipitate of metallic lead was washed with dilute HCl and water. The extent of conversion (q) was determined on the amount of lead obtained. Metallic lead was dissolved in HNO_3 with heating and the solution obtained was used for mass spectrometric analysis.

The isotope abundances were determined using a MI-1201 T mass spectrometer. The statistical error (σ) of the isotopic abundance determination did not in most cases exceed 0.5%. Only for ^{204}Pb was the value of σ found to be about 1%. The isotope abundances in the initial samples were found to be close to those published in the literature.[8]

Some experiments on the γ-radiolysis of Tl^{I} formate solutions were also perfomed. It is known[9] that Tl^{I} is reduced radiolytically to metal under the same conditions as for Pb^{II}. The experimental procedures and analysis of samples were the same as for lead.

The radiation-chemical reduction of Pb^{II} ions in aqueous formate solutions can be described by reactions (1) and (2):

formation of ion-radical products of water radiolysis:

$$H_2O \rightarrow e^-_{aq},\ H,\ OH,\ H^+ \qquad (1)$$

adsorption of OH radicals by formate ions:

$$OH + HCOO^- \rightarrow H_2O + CO_2^- \qquad (2)$$

Since the reduction potentials of e^-_{aq}, H and CO_2^- (–2.9, –2.3 and 2.0 V, respectively) are considerably higher than the redox potential Pb^{II}/Pb^{I} (–1.1–1.5 V),[5,10] Pb^{II} is reduced on γ-irradiation:

$$Pb^{II} + e^-_{aq}(H,\ CO_2^-) \rightarrow Pb^{I} + (H^+,\ CO_2) \qquad (3)$$

followed by Pb^{I} disproportionation:

$$2Pb^{I} \rightarrow Pb^0 + Pb^{II} \quad (k = 8 \times 10^9\ dm^3\ mol^{-1}\ s^{-1})^7 \qquad (4)$$

and nucleation of metal:

$$nPb^0 \rightarrow Pb_n \qquad (5)$$

On changing formate for $Pr^{i}OH$ in reaction (2), alcohol radicals Me_2COH ($E^0 = -1.5$ V) are formed.[10] These radicals take part in the next process,

$$Pb^{I} + Me_2COH \rightarrow [Pb(Me_2COH)]^+ \qquad (6)$$

Metallic lead appears as a result of intermediate transformation in the first-order reaction:

$$n[Pb(Me_2COH)]^+ \rightarrow Pb_n + nMe_2CO + nH^+ \qquad (7)$$

The mechanism of γ-radiolytic reduction of Tl^{I} in formate solutions includes one-electron charge transfer:

$$Tl^{I} + e^-_{aq}(H, CO_2^-) \rightarrow Tl^0 + (H^+, CO_2) \qquad (8)$$

followed by nucleation of metallic thallium.

Table 1 Isotope ratios $R(\sigma)$ and conversion degree q for metallic lead precipitated from irradiated solution.

Organic component	q	$R(\sigma)$		
		$^{208/207}Pb$	$^{208/206}Pb$	$^{208/204}Pb$
HCOONa:				
0.01 mol dm^{-3}	0.47	2.433(16)	2.131(10)	37.77(39)
0.1 mol dm^{-3}	0.51	2.424(12)	–	–
$Pr^{i}OH$:				
0.1 mol dm^{-3}	0.50	2.381(15)	2.086(14)	–
$R_0(\sigma)$	–	2.375(14)[a]	2.079(12)[a]	36.54(40)[a]
		2.382(20)[b]	2.051(16)[b]	36.92(46)[b]

[a] Initial isotope ratios measured in this work. [b] Data from ref. 8.

The results of the experiments are presented in Table 1. From the data obtained it follows that metallic lead, precipitating from formate solution, is enriched by heavy isotopes. In the system with $Pr^{i}OH$ the isotope effect does not exceed the error of isotope abundance determination. Also, the isotope effect is not observed in the radiolytic reduction of Tl^{I}. Thus, for natural thallium the ratio $^{205/203}Tl$ was found to be 2.391(8), and for metallic thallium obtained in accordance with process (8) at $[Tl^{I}]_0 = 0.01$ mol dm^{-3}, $[HCOONa]_0 = 0.1$ mol dm^{-3} and $q = 0.5$ the $^{205/203}Tl$ ratio was 2.387(9).

Table 2 Values of α for lead isotopes.

Organic component	α		
	$^{208/207}Pb$	$^{208/206}Pb$	$^{208/204}Pb$
HCOONa:			
0.01 mol dm^{-3}	1.034	1.036	1.046
0.1 mol dm^{-3}	1.031	–	–
Pr^iOH:			
0.1 mol dm^{-3}	< 1.004	< 1.005	–

The values of α for system with Pb^{II} were calculated according to equation (9):[11]

$$\alpha = \ln(1 - R/R_0 q) \quad (9)$$

The results of the calculation are presented in Table 2.

It can be supposed that the isotope effect observed is determined by the process of Pb^I disproportionation. At radiolytic reduction of Pb^{II} in Pr^iOH media and also on reduction of Tl^I the intermediate valency state disproportionation stage is absent and a significant isotope effect is not observed.

In the literature the question of a possible magnetic isotope effect in the redox reactions of heavy elements is discussed. It is supposed that the isotope effects in some processes of uranyl photochemical reduction[12–14] deal with the nuclear magnetic moment of ^{235}U. Isotope ^{207}Pb possesses a nuclear magnetic moment. However, an anomalous isotope effect for ^{207}Pb did not appear in the system studied. Nor was an isotope effect observed for magnetic nuclei ^{203}Tl and ^{205}Tl. The non-magnetic nature of the observed isotope effect is confirmed by the dependence of α on the isotope mass difference of lead.

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