## CONCLUSIONS

The dissociation constnats of cyclic oxygen-containing phosphorus acids in absolute alcohol were measured by potentiometric titration in charge transfer circuits.

For acyclic phosphorus acids ABPOOH, there is a Brönsted dependence in  $pK(EtOH) \rightarrow pK(H_2O)$ coordinates, which does not apply to 1,3-alkylenephosphoric acids, while in the pK(MeNO2)pK(EtOH) coordinates there is a uniform Brönsted dependence for all the acids.

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REACTIVITY OF LANTHANIDE AND ACTINIDE IONS AT THEIR LOWEST OXIDATION LEVEL WITH C12, Br2, AND 12 IONS IN AQUEOUS SOLUTION AS DETERMINED BY PULSE RADIOLYSIS

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There has been relatively little research on the reactivity of metal ions with free inorganic radicals (Cl2, Br2, I2, NO3, HSO4, SO4, etc.) in aqueous solution, especially in concentrated solutions. Since such information is important in radiation chemistry, in the chemical kinetics of fast reactions, and for the prediction of radiochemical processes in some solutions that are employed in practice, we have made a systematic study of the problem. For this purpose, we have employed pulse radiolysis and recorded short-lived particles spectrophotometrically [1-4]. This paper presents data on the reactivity of Cl2, Br2, and I2 with lanthanide and actinide ions at their lowest oxidation levels [Eu(II), Yb(II), Sm(II), U(III), Np(III), and Pu(III)].

## EXPERIMENTAL

Rate constants were measured with fast-response microsecond- and nanosecond-range spectrophotometric installations based on a U-12 linear electron accelerator (energy E = 5 MeV, pulse length  $\tau = 2.3 \mu sec$ ) and an Élektronika linear accelerator (E = 8 MeV,  $\tau = 15$  nsec).

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Solutions of Eu(III), Yb(III), and Sm(III) were prepared from c.p.- and a.r.-grade salts, c.p.grade acids, and double-distilled water. Eu(II), U(III), Np(III), and Pu(III) were prepared by reducing Eu (III), U(IV), Np(IV), and Pu(IV) with Zn amalgam and by electrolysis. It was shown that the small quantity of Zn ions going into the solution had no effect on the kinetics of the disappearance of the inorganic radicals. The solutions were saturated with Ar and prepared in the cells directly before they were irradiated. The concentration of U(III), Np(III), Pu(III), and Eu(II) was determined on a Specord UV-VIS spectrophotometer. To prevent photolytic transformations in the pulse radiolysis devices, we used BS-5, BS-7, and OS-14 light filters, which absorb the 340, 360, and 540-nm wavelengths, respectively. Optical density changes were registered at 350 to 400 nm for  $Cl_2$ , 360 to 420 nm for  $Br_2$ , and at 725 nm for  $I_2$ . The dose per pulse, determined by the rhodanide method, was (0.5 to 2.5)•10<sup>17</sup> eV/g.

#### DISCUSSION OF RESULTS

The rate constants (RC) of reactions of  $Br_2$  and  $I_2$  radicals with Eu(II), Yb(II), and Sm(II) were determined with Ar-saturated solutions containing 0.9 mole/liter LiClO<sub>4</sub>, 0.1 mole/ liter NaBr or NaI, and 0.01 to 0.04 mole/liter of Eu(III), Yb(III), and Sm(III) salts. The reactivity of Eu(II) with  $Cl_2$  was studied in Ar-saturated solutions containing 0.33 mole/ liter EuCl<sub>3</sub> and 0.01 mole/liter HCl. In all these solutions,  $e_{aq}$  reacts with the lanthanide ions, M(III), and the OH radicals react with the halide ions, X:

$$e_{\rm ag}^{-} + M(\rm III) \rightarrow M(\rm II) \tag{1}$$

$$OH + X^{-} + H^{+} \rightarrow X + H_{2}O$$
<sup>(2)</sup>

$$X + X^{-} \rightarrow X_{2}^{-} \tag{3}$$

Reactions (1)-(3) have a high rate under the conditions of our study. Thus, the RC for the reaction (1) was higher than  $10^{10}$  liters/mole·sec for Eu(III), Yb(III), and Sm(III) ions [5]. The RC for reactions (2) and (3) is close to  $10^{10}$  liters/mole·sec [5, 6], and therefore reactions (1)-(3) are over during the time of one pulse. Consequently, after the pulse, the solution contains M(II) and X<sub>2</sub> in about equal amounts (the e<sub>aq</sub> and OH yield per 100 eV are 3.05 and 2.95, respectively at pH 0 to 2, and 2.8 to 2.9 at pH 4 to 9 [7]).

We can neglect the reaction of M(II) with the  $H_2O_2$  that is formed or with water, and also that of Eu(II) with H<sup>+</sup>, within the time range that we used (the RC for oxidation of Eu-(II) ions by  $H_2O_2$  is <10<sup>4</sup>, that of Yb(II) is <9.1•10<sup>5</sup>, and that of Sm(II) is <6.7•10<sup>7</sup> liters/ mole•sec [8]; even with Sm(II), the RC with water is ~5•10<sup>3</sup> sec<sup>-1</sup> [8]; and Eu(II) is stable in the absence of oxidizing agents). Consequently,  $X_2^-$  should disappear in the course of two second-order reactions:

$$X_2^- + X_2^- \rightarrow X_2 + 2X^- \tag{4}$$

$$X_2^- + M(II) \rightarrow M(III) + 2X^-$$
(5)

The RC of reaction (4) with  $Br_2^-$  and  $I_2^-$  were determined in the same solutions, but without M(III) and saturated N<sub>2</sub>O, and were equal to 6.10° and 9.10° liters/mole.sec, respectively. For Cl<sub>2</sub>, the value of 2k<sub>4</sub> (3.7.10° liters/mole.sec) was taken from [9].

Calculations of  $k_5$  were made on an Iskra-226.6 microcomputer by numerical integration of the following system of differential equations:

$$d [X_2^-]/dt = -2k_4 [X_2^-]^2 - k_5 [X_2^-][M(II)]$$
(6)

$$d \,[\mathrm{M(II)}]/dt = -k_5 \,[\mathrm{X}_2^{-}][\mathrm{M(II)}] \tag{7}$$

and minimizing the mean-square deviations between the experimental and calculated values of the optical density of the  $X_2$  absorption band during the course of the process [accounting also for the absorption of M(II) and M(III)].

The disappearance of  $I_2$  in solutions containing Eu(III) ions occurs at practically the same rate as it does when those ions are absent; i.e., the rate of the reaction between  $I_2$  and Eu(II) is lower than the disproportionation rate of  $I_2$ . Therefore, the value of  $k[I_2 + Eu(II)]$  was measured in solutions containing different quantities of Eu(II) obtained by reducing Eu(III) with Zn amalgam. The values of  $k_s$  found are shown in Table 1. This table also lists known RC values for Cr(II) and V(II) [10] for comparison purposes. The RC of the reactions of  $Cl_2$  with Sm(II) and Yb(II) were not determined because conversion of the OH radicals to  $Cl_2$  is not quantitative in the body of the solution if it is neutral or close to

TABLE 1. Rate Constants for the Reactions of  $Cl_2$ ,  $Br_2$ , and  $I_2$  with Metal Ions at Low Oxidation Levels

Metal ion	Ion-radical	k, liters/ mole • sec	Metal ion	Ion-radical.	k, liters/ mole.sec
Eu (II)	$\begin{bmatrix} CI_2^- \\ Br_2^- \\ I_2^- \end{bmatrix}$	$ \begin{vmatrix} (5.0\pm0.7)\cdot10^9 \\ (1.0\pm0.2)\cdot10^9 \\ (9.0\pm1.0)\cdot10^7 \end{vmatrix} $	Pu(III)	$\begin{array}{c c} Cl_2^{-} & (3) \\ Br_2^{-} & (4) \\ \end{array}$	$(3.0\pm0.3)\cdot10^7$ $(1.6\pm0.2)\cdot10^8$
Yb(II)	$\operatorname{Br}_2^-$ I <sub>2</sub> <sup>-</sup>	$(5.0\pm0.7)\cdot10^9$ $(5.5\pm0.8)\cdot10^9$	Cr(11) *	$\begin{bmatrix} CI_2^-\\ Br_2^-\\ I_2^- \end{bmatrix}$	$\begin{array}{c} (2.4\pm0.3)\cdot10^9\\ (1.9\pm0.2)\cdot10^9\\ (1.5\pm0.2)\cdot10^9\end{array}$
Sm(II)	$\mathrm{Br_2^-}_{\mathrm{I_2^-}}$	$\begin{array}{c} (7.5 \pm 1.0) \cdot 10^9 \\ (6.5 \pm 1.0) \cdot 10^9 \end{array}$	V(II) *	$Cl_2^-$ $Br_2^-$	$(1.95\pm0.2)\cdot10^{4}$ $(1.48\pm0.2)\cdot10^{4}$ $(1.43\pm0.2)\cdot10^{4}$
U(III)	I2 <sup>-</sup>	(1,2±0,1) ·10 <sup>9</sup>		12	(1.10-0.2) 10
Np(III)	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\left \begin{array}{c} (1.6\pm0.1)\cdot10^9\\ (1.1\pm0.1)\cdot10^8\\ (5.0\pm0.5)\cdot10^6\end{array}\right $			

\*Constants determined with an ionic strength  $\mu = 0.5$ .



Fig. 1. Logarithm of the reaction rate constant (k) for Pu(III) (1), Np(III) (2), and Eu(II) (3) with  $Cl_2$  (a),  $Br_2$  (b), and  $I_2$  (c) ion-radicals vs  $\Delta E^\circ$ ,

neutral and reactions of Sm(II) and Yb(II) with  $H^{+}$  ions as well as reactions in which H atoms participate must be taken into account in an acid medium.

The RC of the reactions of  $X_2$  with actinide ions, M(III)

$$M(III) + X_{2}^{-} \rightarrow M(IV) + 2X^{-}$$
(8)

was determined by the drop in the solution's optical density for the ion-radical's absorption band in the presence of a sufficient amount of actinide ion. The values measured for  $k_8$  are listed in Table 1. It was difficult to determine the RC for reactions of  $Cl_2$  and  $Br_2$  with U(III) because U(IV) is reduced by Zn amalgam very slowly at low concentrations, and at U(IV) concentrations  $\geq 3 \cdot 10^{-3}$  mole/liter the region of the UV spectrum where  $Cl_2$  and  $Br_2$  are absorbed is opaque owing to the absorption of U(III) itself. We were also unable to determine the RC for the reaction of Pu(III) +  $I_2$  because the rate was too low.

The RC values listed in Table 1 indicate that the rate of reactions of  $X_2$  with Yb(II), Sm(II), and Cr(II) are limited by diffusion or are close to the diffusion limit  $k_{dif}$ . An estimate of this limit for the reaction of  $I_2$  with lanthanide M(II) ions, made by the Debye equation, gives a value of ~7.5•10° liters/mole•sec (for  $\mu = 0.1$ ) for  $k_{dif}$  (the diffusion coefficient of  $I_2$  in 0.5 M Na<sub>2</sub>SO<sub>4</sub> is equal to  $1.2 \cdot 10^{-3}$  cm<sup>2</sup>/sec (11) and the radius of  $I_2$  was calculated by the Debye equation from the value of  $2k_4$ ). We can draw a similar conclusion for the reactions of  $Cl_2$  + Eu(II), Br<sub>2</sub> + Eu(II), X<sub>2</sub> + U(III), Cl<sub>2</sub> + Np(III), Cl<sub>2</sub> + V(II), and Br<sub>2</sub> + V(II). The rates of the reactions X<sub>2</sub> + Pu(III), Br<sub>2</sub> + Np(III), I<sub>2</sub> + Np(III), and I<sub>2</sub> + V(II) are much lower than the diffusion limit.

We found a linear dependence of log  $k_6$  vs the difference  $\Delta E^\circ$  for the oxidation-reduction potentials of  $X_2$  /2X and M(IV)/M(III) pairs in the case of Np(III) and Pu(III), i.e., vs the free energy of the reaction (Fig. 1). In this calculation, we used the following values for

the potentials:  $E^{\circ}(Cl_2^{-}/2Cl^{-}) = 2.3 V$ ;  $E^{\circ}(Br_2^{-}/2Br^{-}) = 1.7 V$ ;  $E^{\circ}(I_2^{-}/2I^{-}) = 1 V [12]$ ;  $E^{\circ}(Np-(IV)/Np(III)) = 0.15 V$ ;  $E^{\circ}(Pu(IV)/Pu(III)) = 1 V [13]$ . The dependence we found agrees satisfactorily with the RC of the reactions of  $Br_2^{-}$  and  $I_2^{-}$  with  $Eu(II) [E^{\circ}$  for the Eu(III)/Eu(II) pair is -0.43 V [13]].

We can conclude from the relationships that we found that the oxidation of Np(III) and Pu(III) by X<sub>2</sub> ion-radicals proceeds by a mechanism of electron transfer within the sphere. In that case, when the change in the coordination sphere of the reagents and the electrostatic interaction are the same, the determining factor for the reaction rate is the change in the free energy of the reaction. It can be determined from the relationship we found that the RC for the reaction of Pu(III) with I<sub>2</sub> ( $\Delta E^{\circ} \approx 0$ ) should be equal to  $-6 \cdot 10^{\circ}$  liters/mole·sec and k<sub>6</sub> (and evidently k<sub>5</sub> as well) reach the diffusion limit when  $\Delta E^{\circ} \approx 2.3$  V (i.e., when  $\Delta G \approx -220$  kJ/mole). The reaction of X<sub>2</sub> with divalent lanthanide ions apparently follows a similar mechanism, but then the rate of most of the reactions, except that of Br<sub>2</sub> + Eu(II) and I<sub>2</sub> + Eu(II), is limited by diffusion ( $\Delta E^{\circ} > 2.3$  V).

The value of log k  $[I_2 + U(III)]$  is much higher than the value expected from the correlations that we found. This fact indicates that the U(III) oxidation mechanism is different from that of Np(III) and Pu(III).

### CONCLUSIONS

1. We have measured the rate constants for reactions of lanthanide and actinide ions at their lowest oxidation levels with  $Cl_2^-$ ,  $Br_2^-$ , and  $I_2^-$  ion-radicals.

2. We have shown that the rates of the reactions of Yb(II) and Sm(II) with  $Br_2$  and  $I_2$ , and of Eu(II) with  $Cl_2$  are limited by diffusion, whereas those for the reactions of Np(III) and particularly Pu(III) are below the diffusion limit.

3. We have found that the logarithm of the rate constant for reactions of Np(III) and Pu(III) with  $Cl_2$ ,  $Br_2$ , and  $I_2$ , and also for Eu(II) with  $Br_2$  and  $I_2$ , depends linearly on the free energy of the process.

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