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Kinetics of Oxidation of Iodide by Vanadium (V): Catalysis by the Water Pools of CTAB Reverse Micelles[1]

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Abstract—The kinetic study of the oxidation of iodide ion by V(V) has been carried out in the water pools of cetyl trimethyl ammonium bromide(CTAB) reverse micelles in a mixture of chloroform-hexane (3 : 2). The study of the effect of concentration of V(V) and I^- on rate show that the reaction obeys first order kinetics with each of the reactants. A plot of k' (pseudo first order rate constant) versus $[H^+]$ is linear with a positive intercept at constant concentrations of iodide and bromide. The rate of the reaction is markedly increased in the reverse micellar medium compared to conventional aqueous medium under identical conditions. The pronounced acceleration in reverse micelles has been accounted for by the concentration effect in the water pool which have an effect on kinetics.

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“Water pools” refer to water present in the cavities of reverse micelles which are formed by adding water to surfactant aggregates in non-polar solvents [1–3]. This solubilized water provides a medium with unique properties for reactions involving polar substrates [4–6]. Interactions between the substrate and polar head groups of surfactants are quite strong and specific, so the reverse micelles strongly affect chemical reactions and enzyme reactivity [7–10]. The influence of reverse micelles and the special properties of the water pool depend on a parameter, $W = [H_2O]/[\text{surfactant}]$ [11, 12]. The water pool has much lower polarity and dielectric constant compared to bulk water [13, 14]. In the case of CTAB reverse micelles, the dielectric constant equals to that of methanol-water systems [5]. Another property of the water pool which has effect on rates of reactions is high ionic strength in case of charged surfactants (Na^+ in the case of aerosol-OT and Br^- in the case of CTAB) [6]. For reactions taking place in water pool, other important factor that is responsible for alterations in rates is the favorable partitioning between polar micellar cavity and non polar bulk solvent. If the substrates are highly soluble in entrapped water and have low solubility in bulk phase, then there is enormous concentration effect in the water pool [15]. A quantitative kinetic analysis of reactions in the water pool is difficult because the special properties of the water pool affect the rate simultaneously. In our earlier work in the basic hydrolysis tris-(2,2'-bipyridy)iron(II) complex we found that the effect of ionic strength predominates over other properties of the water pool [16]. With a view to further investigate this aspect we have taken up the study the kinetics of reaction of the oxidation of iodide by V(V) in the water pools of CTAB-hexane-chloroform-water system, which has been well studied in conventional aqueous medium [17]. The results are reported in this paper.

EXPERIMENTAL

Alt solutions were prepared in doubly distilled water and chemicals used were of analytical grade. Hexane and chloroform were distilled before use. Sodium Vanadate solution was prepared and standardized according to the procedure of Gopala Rao et al. [18]. The iodide was prepared by dissolving the requisite amount of potassium iodide (E. Merck) in water and standardized with standard silver (I) nitrate solution using a potentiometric end point.

Preparation of Reverse Micellar System and Initiation of the Reaction

A typical experiment was carried out as follows: A solution of CTAB was prepared in a mixture of chloroform and hexane (3 : 2) to obtain a concentration of 0.1 mol dm^{-3}. Small quantities of aqueous solutions of iodide and acid (0.025–0.3 cm^3) were injected into 10 cm^3 of CTAB solution using a micro pipette. Vanadium (V) solution was added in the end to initiate the reaction. These mixtures were shaken sufficiently to obtain a transparent and apparently homogenous solution that can be regarded as a reverse micellar system. In all the experiments the molar ratio of [water] to [CTAB] = W was varied from 4.16 to 16.6.

The reactions were monitored by measuring the absorbance of the triiodide at 355 nm under the con-

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ditions $[I] \gg [V(V)]$,(ε = 20.000 dm^{-3} mol^{-1} cm^{-1}) using Milton–Roy (spectronic1201) spectrophotometer with thermostated cell compartment. Pseudo first order rate constants were obtained from slopes of log (absorbance) versus time plots. The kinetic data are the averages from triplicate runs with reproducibility of ±5%.

CALCULATION OF EFFECTIVE CONCENTRATIONS IN REVERSE MICELLES:

In the studies of reactions in reverse micelles involving water-soluble reactants, the reactivity in the aqueous droplets of the reverse micelle is usually compared with that in bulk aqueous medium. In the case of first order reactions the measured rate constants (units-s^{-1}) may be compared directly in the two types of systems. However, in the case of bimolecular processes, the calculation of the second order rate constant (units-dm^3 mol^{-1} s^{-1}) involves consideration of the concentration of species in the reverse micelle and the question arises as to whether the overall concentration or the concentration in water pool should be employed. Hence, a concentration scale has to be defined in order to interpret the data in terms of a comparison of reactivity in reverse micelle and bulk solvent media. In all the investigations carried out, the reactions take place only in the water pools, in which the reactants are constrained. The kinetic data has to be analyzed taking only their effective concentrations in the water pool but not their overall concentrations in the reverse micellar system as a whole. The effective concentrations of the reactants which are not soluble in the organic phase and also not bound in the interface between micellar surface and water in the water pool have been calculated by dividing the overall concentration by the volume fraction of solubilized water, f [15]. The volume fractions lie in the range (7.44–29.0) × 10^{-3} for 0.1 mol dm^{-3} CTAB. Hence there is (30–130)-fold increase in concentrations. For example, if the concentration of CTAB is 0.1 mol dm^{-3}, $W = 4.16$, $f = (0.0744/10)$ and $[H^+]_{overall} = 0.95 \times 10^{-3}$ mol/l then $[H^+]_{eff} = \{[H^+]_{overall}/f\} = \{0.95 \times 10^{-3}/0.00744\} = 0.127$ mol/l. From now onwards, the subscript "o" is used to represent overall concentrations and subscript "e" to represent effective concentrations.

RESULTS AND DISCUSSION

The kinetics of the reaction has been investigated in the presence of CTAB reverse micelles in the chloroform-hexane mixtures varying the overall concentration of V(V) in the range, (3.0–10.0) × 10^{-5} mol dm^{-3} and I^- in the range, (1.5–10.0) × 10^{-4} mol dm^{-3}. The overall hydrogen ion concentration is varied from 0.95 × 10^{-3} to 5.02 × 10^{-3} mol dm^{-3}; thus the corresponding effective concentrations are in the range (0.096–0.507) mol dm^{-3}. At these hydrogen ion concentrations, V(V) [19–24] is known to exist entirely in the form of VO_2^+. The values of pseudo first order rate constant, k', have been determined at different hydrogen ion concentrations and plotted against $[H^+]_{eff}$. The plot is linear with a positive intercept on the k'-axis showing that the reaction mechanism involves two different rate determining steps, one with a rate independent of $[H^+]_{eff}$ accounting for the positive intercept in the plot and the other with a rate directly proportional to effective hydrogen ion concentration. The hydrogen ion acceleration with linear dependence of rate on $[H^+]_{eff}$ and [vanadium(V)] is due to the formation of $V(OH)_3^{2+}$ according to the Equilibrium [25]:

$$VO_2^+ + H_3O^+ \xrightleftharpoons{K_1} [V(OH)_3]^2.$$

The more positively charged $[V(OH)_3]^{2+}$ is a better oxidant compared to VO_2^+ [26]. Thus the reaction involves the species, VO_2^+, $V(OH)_3^{2+}$, and I^-. These ions can be expected to be constrained in the water pool and cannot be present in the organic phase. Further, the reaction rate increases in the presence of Br^- and k' has been found to be directly proportional to $[Br^-]$ in the aqueous medium and the bromide ion acceleration can be ascribed to the formation of $\{VO_2Br\}$ and $\{V(OH)_3Br^+\}$ and these species rather than VO_2^+ or $V(OH)_3^{2+}$, are the active oxidizing species. The plot of k' versus $[Br^-]$ is linear without any intercept on k'-axis showing that the bromide-ion independent paths involving VO_2^+ and $[V(OH)_3]^{2+}$ can be neglected. Thus, the following mechanism accounts for the kinetics and results.

$$VO_2^+ + H_3O^+ \xrightleftharpoons{K_1} [V(OH)_3]^{2+}, \tag{I}$$

$$VO_2^+ + Br^- \xrightleftharpoons{K_2} VO_2Br, \tag{II}$$

$$V(OH)_3^{2+} + Br^- \xrightleftharpoons{K_3} [V(OH)_3Br]^+, \tag{III}$$

$$VO_2Br + I^- \xrightarrow{k_1} I + V(IV) + Br^-, \tag{IV}$$

$$[V(OH)_3Br]^+ + I^- \xrightarrow{k_2} I + V(IV) + Br^-, \tag{V}$$

$$I + I^- \xrightarrow{\text{fast}} I_2.$$

The rate law for this scheme is given by the equation

$$-\frac{d}{dt}[V(V)] = k_1K_2[VO_2^+]_{eff}[Br^-]_{eff}[I^-]_{eff} + k_2K_1K_3[VO_2^+]_{eff}[Br^-]_{eff}[I^-]_{eff}[H^+]_{eff}$$

or the pseudo first order rate constant, k', is given by

$$k' = k_1K_2[Br^-]_{eff}[I^-]_{eff} + k_2K_1K_3[Br^-]_{eff}[I^-]_{eff}[H^+]_{eff}. \tag{1}$$

Replacing k_1K_2 by k_4', and k $k_2K_1K_3$ by k_4''

$$k' = k_4'[Br^-]_{eff}[I^-]_{eff} + k_4''[Br^-]_{eff}[I^-]_{eff}[H^+]_{eff}. \tag{2}$$

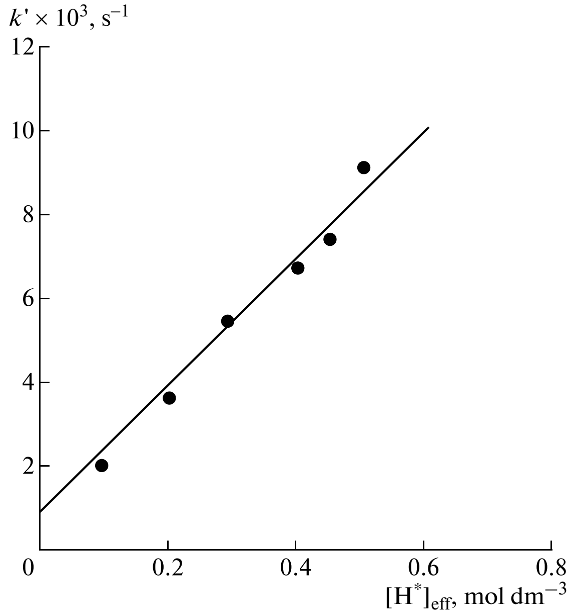
Effect of Variation of W on Rate

The pseudo first order rate constant determined in the reverse micelle at the same concentration of V(V), I^-, H^+, and Br^- is 170 times higher than in the aqueous medium under identical conditions as shown below:

$$[V(V)]_0 = 5.0 \times 10^{-5}\ \text{mol dm}^{-3};$$
$$[I^-]_0 = 7.5 \times 10^{-4}\ \text{mol dm}^{-3};$$
$$[H^+]_0 = 3.75 \times 10^{-3}\ \text{mol dm}^{-3};$$
$$[Br^-]_{eff} = 3.3\ \text{mol dm}^{-3};$$
$$T = 30 \pm 0.1°\text{C}.$$

k'_{aq}, s^{-1}	$k'_{rev.mic}$, s^{-1}($W = 16.6$)	$k'_{rev.mic}/k'_{aq}$
1.41×10^{-6}	2.4×10^{-4}	170

To examine whether the effect of variation of W on rate can be quantitatively analyzed considering only concentration changes due to change in W, it is necessary to consider the changes in the concentrations of the species brought about by the variation of W. They are the concentrations of V(V), I^-, H^+, and Br^-. The study of effect of concentrations of V(V) and I^- on rate showed that the reaction obeys simple first order kinetics with respect to each of these reactants. However, the effect of change of bromide ion concentration on rate in the water pool could not be investigated because extraneous addition of Br^- has resulted in the instability of the reverse micelle and in the aqueous medium, the rate is directly proportional to $[Br^-]$. Since a plot of k' versus $[H^+]_{eff}$ is linear with a positive intercept at constant $[Br^-]_{eff}$ and $[I^-]_{eff}$, (figure) the slope giving the specific rate constant of H^+ ion-dependent path (k''_4) and intercept giving the specific rate constant of H^+ ion-independent path (k'_4). The rate constant of H^+ ion-dependent path (k''_4) and H^+ ion-independent path (k'_4) have been found to be 15.0×10^{-3} $dm^9\ mol^{-3}\ s^{-1}$ and 0.9×10^{-3} $dm^6\ mol^{-2}\ s^{-1}$, respectively. Using these values of k''_4 and k'_4, the value of the pseudo first order rate constant, k' has been calculated for the kinetic data at different W and at different CTAB concentrations (0.1, 0.2, and 0.3 $mol\ dm^{-3}$) and compared with the pseudo first order rate constant, k', obtained experimentally. The data is presented in table and shows that the observed and calculated rate constants are in good agreement with each other. This also shows that the rates can be predicted with good accuracy by taking only concentration effect with change in W. The reason for this is due to the cancellation of effects due to change in the special properties of the water pool with change in W. As W increases, the ionic strength decreases, but the dielectric constant increases. The two have opposing effects if one examines various steps determining the rates of the reaction in the mechanism. The constant for equilibrium (1) involving only cations decreases with decrease in ionic strength but increases with increasing dielectric constant as W increases. The equilibrium constant of the step (2) involving cations and anions increases with decrease in ionic strength whereas it decreases with increase in dielectric constant as W increases. The equilibrium constant of step (3) undergoes similar changes with decreasing ionic strength and increasing dielectric constant. The rate constants k_1 and k_2 again increase with decrease in ionic strength but decrease with increase in dielectric constant as W increases. Thus, the combination of these opposing effects in all the steps appear to give a resultant effect; which is much smaller than the concentration effect with change in W. Thus, the effect of W on rate finally turns to be a mere concentration effect, all specific effects of the water pool canceling.



A plot of k' vs $[H^+]_{eff}$ for the oxidation of iodide by V(V); $[V(V)]_0 = 3.8 \times 10^{-5}$ mol dm^{-3}; $W = 5.5$; $T = 30 \pm 0.1°C$ $[I^-]_0 = 9.65 \times 10^{-4}$ mol dm^{-3}; CTAB = 0.1 mol dm^{-3}.

The hydrogen ion dependence of rate is different in the CTAB water pools from that observed by Radhakrishnamurthi et al. [4] in the conventional aqueous perchloric acid medium. In the former case, there is linear dependence between rate and H^+ ion whereas in the uncatalyzed reaction the rate-law has $[H^+]^2$ term. It may be noted that in the former case, the reaction is bromide ion catalyzed, the catalysis being due to the formation of the intermediate complex VO_2Br or $V(OH)_3Br^+$. Interestingly, in the case of other catalyzed oxidation of iodide ion by vanadium (V) in aqueous perchloric acid medium (oxalic acid catalysis) Subba Rao et al. [27] reported a first order dependence of rate on H^+ ion concentration. In this case, the catalytic effect is traced to the formation of

Observed and calculated rate constants for the oxidation of iodide by V(V)

CTAB, mol dm^{-3}	W	$f \times 10^3$ (volume fraction)	$k_{obs} \times 10^3$, s^{-1}	$k^*_{calc} \times 10^3$, s^{-1}
0.1	4.16	7.44	9.06	11.84
	5.50	9.90	4.80	4.98
	6.94	12.30	2.61	3.02
	9.72	17.20	1.12	1.04
	12.50	22.00	0.55	0.52
	16.60	29.12	0.24	0.24
0.2	4.16	14.78	3.14	3.18
	5.50	19.60	1.41	1.44
	6.94	24.39	0.79	0.79
	9.72	33.80	0.33	0.32
	12.50	43.10	0.19	0.17
	16.60	56.60	0.09	0.083
0.3	4.16	22.00	1.51	1.57
	5.50	29.12	0.75	0.73
	6.94	36.14	0.44	0.47
	9.72	49.88	0.19	0.17
	12.50	63.20	0.085	0.094
	16.60	82.60	0.041	0.047

Note: The overall concentration of $[Br^-]$ is the stoichiometric concentration of CTAB. $[I^-]_0 = 7.5 \times 10^{-4}$ mol dm^{-3}; $[V]_0 = 5.0 \times 10^{-5}$ mol dm^{-3}; $[H^+]_0 = 3.75 \times 10^{-3}$ mol dm^{-3}; $T_{emp} = 30 \pm 0.1$°C, $k''_4 = 15.0 \times 10^{-3}$ dm^9 mol^{-3} s^{-1}, $k'_4 = 0.90 \times 10^{-3}$ dm^6 mol^{-2} s^{-1}.

$* k_{calc} = k'_4\{[Br^-]_0/f\}\{[I^-]_0/f\} + k''_4\{[Br^-]_0/f\}\{[I^-]_0/f\} \times \{[H^+]_0/f\}$.

the more reactive 1 : 1 complex between $V(OH)_3^{2+}$ and oxalic acid, the former being in equilibrium with VO_2^+.

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