

## Aquation of (Dimethyl sulphoxide)pentaamminecobalt(III) in Aqueous Cetyltrimethylammonium Bromide Solutions

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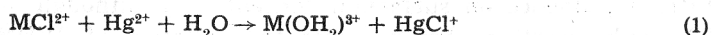
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The rate of aquation of  $[\text{Co}(\text{NH}_3)_5(\text{DMSO})]\text{Br}_3$  was measured in solutions containing the surfactant cetyltrimethylammonium bromide (CTAB) over the concentration range  $9.55 \times 10^{-4}$  mol  $\text{dm}^{-3}$  to 0.450 mol  $\text{dm}^{-3}$ . This large change in CTAB concentration affected the rate very little and no significant amounts of  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$  were formed. It was concluded that, if  $\text{Br}^-$  counterions were concentrated in the microregions around the positively charged CTAB micelles, then there was no corresponding increase in the formation of  $\text{Co}(\text{NH}_3)_5(\text{DMSO})^{3+}$ .  $\text{Br}^-$  ion-pairs in this region with subsequent  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$  formation.

For several years we have been interested in the effects of solvent composition on rates of inorganic substitution reactions. We have found<sup>1</sup> that the rate of aquation of  $\text{M}(\text{DMSO})^{3+}$  ( $\text{M} = \text{Co}(\text{NH}_3)_5$  and  $\text{DMSO} =$  dimethyl sulphoxide) in ethanol-water-perchlorate media over a wide range of solvent compositions was independent of ionic strength and of the nature of the cation ( $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ) in the perchlorate compound employed; it was dependent on the  $\text{ClO}_4^-$  concentration and on the ethanol: water ratio. Also, the activation enthalpy was independent of solvent composition within a small error of approximately 1 percent. This was interpreted to mean that increasing  $\text{ClO}_4^-$  and ethanol contents displaced water from the solvation shell of  $\text{M}(\text{DMSO})^{3+}$  increasing the extent of internal return of DMSO. Similar results were found in other mixed solvents<sup>2</sup>. Solvent interchange results for  $\text{M}(\text{OH}_2)^{3+}$  and  $\text{M}(\text{DMF})^{3+}$ , where DMF = dimethylformamide, were interpreted<sup>3</sup> in terms of a specific interaction between DMF molecules in coordinated and bulk phase sites. As an extension of these investigations it was of interest to study the aquation of  $\text{M}(\text{DMSO})^{3+}$  in solutions of a surfactant, cetyltrimethylammonium bromide (CTAB).

It has been found<sup>4</sup> that the rate of reaction (1) was dramatically increased



by the presence of  $5 \times 10^{-5}$  N polyvinylsulfonic (PVS) acid. The reason offered to explain this result was that the PVS concentrated the two cationic reactants

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in microregions surrounding the PVS polyions. To a significant degree micelles should function like polyions: the charged outer surface of a micelle (say, the positively charged outer surface of a CTAB micelle) should attract a high density of counterions (say,  $\text{Br}^-$  ions). Because<sup>5</sup>  $\text{M}(\text{DMSO})^{3+}$  forms ion-pairs with  $\text{Br}^-$  it is possible that in the microregions surrounding the micelles there would be increased ion-pair formation of  $\text{M}(\text{DMSO})^{3+} \cdot \text{Br}^-$  with subsequent increased anation to form  $\text{MBr}^{2+}$ . Here we report the results of kinetic studies with  $[\text{M}(\text{DMSO})]\text{Br}_3$  in CTAB solutions.

## RESULTS AND DISCUSSION

The rate of disappearance of  $\text{M}(\text{DMSO})^{3+}$  in these aqueous CTAB solutions was first-order for all solutions used. The observed first-order rate constants,  $k_{\text{obs}}$ , are listed in Table I as a function of surfactant concentration. The

TABLE I

Aquation Rate Constants for  $[\text{M}(\text{DMSO})]\text{Br}_3$  in CTAB Solutions.  $1.00 \times 10^{-3}$  mol  $\text{dm}^{-3}$  Total  $\text{Co}(\text{III})$ .  $0.0100$  mol  $\text{dm}^{-3}$   $\text{HBr}$ .

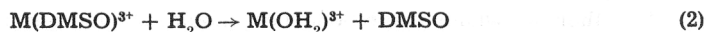
CTAB/mol $\text{dm}^{-3}$	$t/^\circ\text{C}^a$	$10^4 k_{\text{obs}}^b/\text{s}^{-1}$
	45.00	2.36
$0.955 \times 10^{-3}$		2.36
$2.52 \times 10^{-3}$		2.36
$3.80 \times 10^{-3}$		2.40
$4.94 \times 10^{-3}$		2.37
$1.00 \times 10^{-2c}$		2.41 <sup>c</sup>
$1.50 \times 10^{-2}$		2.40
$3.00 \times 10^{-2}$		2.44
0.1000		2.44
0.2000		2.48
0.3000		2.50
0.4500		2.57
	35.00	0.609
$3.797 \times 10^{-3}$		0.618
$2.996 \times 10^{-2}$		0.620
0.2500		0.622
0.4000		0.626

<sup>a</sup>  $\pm 0.05$   $^\circ\text{C}$

<sup>b</sup> All rate measurements performed in duplicate. Error in  $k_{\text{obs}}$  approximately 1 percent.

<sup>c</sup> An average of  $k_{\text{obs}} = (2.30 \pm 0.20) \times 10^{-4} \text{ s}^{-1}$  was obtained from 8 separate kinetic experiments employing a Beckman DU spectrophotometer with a cell compartment thermostated at  $(45.0 \pm 0.1)^\circ\text{C}$  and a wavelength of 518 nm. These  $k_{\text{obs}}$  values have a larger error because of the much smaller absorbance change at 518 nm as compared to 290 nm.

rate constants  $k_{\text{obs}}$  were independent of  $\text{H}^+$  concentration so the latter was maintained constant at  $0.010$  mol  $\text{dm}^{-3}$ . It is seen that the  $k_{\text{obs}}$  show very little dependence on surfactant concentration although micelles are present<sup>6</sup>. The only reaction observed was the aquation of  $\text{M}(\text{DMSO})^{3+}$  as shown in reaction (2). There was, at most, only a small amount of  $\text{MBr}^{2+}$  formation. Had the ion-pairs concentrated in the micro-



regions around micelles there should have been a significant amount of  $\text{MBr}^{2+}$  formed. The reasons for this statement are: (1)  $\text{MBr}^{2+}$  undergoes solvolysis more slowly than  $\text{M}(\text{DMSO})^{3+}$  undergoes anation by  $\text{Br}^-$  so that  $\text{MBr}^{2+}$  would accumulate in solution to some extent. (2) About 75 percent of the ion-pairs  $\text{M}(\text{DMSO})^{3+} \cdot \text{Br}^-$  in DMSO undergo anation by  $\text{Br}^-$  rather than solvent exchange<sup>5</sup>. In purely aqueous solutions about 20 percent of the ion-pairs  $\text{M}(\text{OH}_2)^{3+} \cdot \text{Br}^-$  undergo anation since anation occurs at approximately one-fifth the rate of solvent exchange<sup>7</sup>. Therefore a minimum of approximately 20 percent of all ion-pairs formed in the microregions around CTAB micelles should be undergoing anation reactions and forming  $\text{MBr}^{2+}$  as product. Since we did not observe any significant  $\text{MBr}^{2+}$  formation throughout the reaction we must conclude that there was not a marked increase of ion-pairs in the microregions surrounding the CTAB micelles even if there was a high concentration of  $\text{Br}^-$  ions in these regions.

In aqueous solutions at 25 °C the formation constants<sup>8</sup> for the bromo-complex given by equation (3) is not markedly temperature-dependent and con-

$$K_f = \frac{[\text{MBr}^{2+}]}{[\text{MOH}_2^{3+}] [\text{Br}^-]} = 0.3 \quad (3)$$

sequently would be expected to have approximately the same value at 35 and 45 °C. Since total bromide ion concentration was 0.013 mol dm<sup>-3</sup>, only about 0.4 percent of  $\text{MBr}^{2+}$  at most would be expected to form unless kinetic control via ion-pair formation in regions of high  $\text{Br}^-$  concentration produced larger amounts of  $\text{MBr}^{2+}$ . This is substantially less than the approximately 1 percent of  $\text{MBr}^{2+}$  that could have been detected and explains the absence of  $\text{MBr}^{2+}$  in the reaction mixtures.

We were unable to study this reaction in reversed micelles since addition of benzene or toluene to the solutions produced precipitation.

#### EXPERIMENTAL

**Materials.** The  $\text{Co}(\text{NH}_3)_5(\text{DMSO})^{3+}$  complex in DMSO was prepared by the method of Mac-Coll and Beyer<sup>9</sup>. The bromide salt was prepared by addition of a saturated NaBr solution in methanol to the solution containing the freshly prepared  $\text{Co}(\text{NH}_3)_5(\text{DMSO})^{3+}$  ion. The purple crystals were washed with cold water, ethanol and ether and dried over silica gel. Analysis: Calculated for  $[\text{Co}(\text{NH}_3)_5(\text{DMSO})] \text{Br}_3$ : Co, 12.75; Br, 51.90. Found: Co, 12.52 Br, 51.63. From thermogravimetric analysis: Calculated  $\text{Co}_3\text{O}_4$ , 17.4; Found, 18.2. All the rest of the chemicals were reagent grade.

**Procedures.** Most of the kinetic data were taken in aqueous media with a Unicam SP 500 spectrophotometer at a wavelength of 290 nm. The temperature of a reaction mixture was maintained within  $\pm 0.05$  °C by a water bath. Plots of  $\log(A_t - A_\infty)$ , where the  $A$ 's are the absorbances at time  $t$  and infinite time, respectively, against time were linear for several half-lives. Kinetic measurements made at wavelength of 518 nm with a Beckman DU spectrophotometer having a thermostated cell compartment were not significantly different from the measurements made at 290 nm.

Analyses were made for  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$  formation by passing various reaction mixtures containing the surfactant, CTAB, at various stages of completion of the reaction through a Dowex 50W-X4, 100–200 mesh, column in hydrogen form which adsorbed the complex cations. The bromo-complex was readily eluted by 2 mol dm<sup>-3</sup>  $\text{HClO}_4$  but the aquo- and dmsu-complexes were not. About 1% of bromo-complex could have been readily detected.

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## SAŽETAK

**Akvacija (dimetilsulfoksid)pentaaminkobalta(III) u rastvorima  
cetiltrimetilamonium bromida**

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Mjerena je brzina akvacije  $[\text{Co}(\text{NH}_3)_5(\text{DMSO})]\text{Br}_3$  u rastvorima koji su sadržavali površinski aktivnu supstancu cetiltrimetilamonium-bromida (CTAB) u području koncentracija od  $9.55 \times 10^{-4}$  mol dm<sup>-3</sup> do 0.450 mol dm<sup>-3</sup>. Ta velika promjena u koncentraciji CTAB vrlo malo je utjecala na brzinu i nisu bile stvorene znatnije količine  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ . Zaključeno je da, ako su se  $\text{Br}^-$  protujoni koncentrisali u mikropodručjima oko pozitivno nabijenih micela CTAB, onda nije bilo odgovarajućeg povećanja stvaranja jonskih parova  $\text{Co}(\text{NH}_3)_5(\text{DMSO})^{3+} \cdot \text{Br}^-$  u tom području uz naknadno stvaranje  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ .

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