trans–cis Isomerization of *trans*-Bis(oxalato)diaquachromate(III) in Aqueous Solutions of Ethanol and tert-Butanol

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The *trans–cis* isomerization of *trans*-bis(oxalato)-diaquachromate(III) in aqueous solutions is believed to occur via a five-membered coordination species with an oxalate ion acting as a unidentate ligand, followed by exchange in position between the open-end of the oxalate ligand and an adjacent water ligand. For both uncatalysed [1] and cation-catalysed [2, 3] pathways, this mechanism was believed to operate. In neutral to basic media also, the same mechanism was suggested, except that the reactant and the product contain corresponding hydroxy complexes due to hydrolysis [4]. The implication inherent in this mechanism is that the solvent water does not play a role in the rate-determining step. This can generally be checked by the lack of an isotope effect when the isomerization is allowed to take place in D_2O. As shown below, the observed rates in H_2O and D_2O were indeed the same within experimental error.

On the other hand, the effect of mixed aqueous solvents, particularly those with alcohols, on the solvolytic reactions of coordination complexes has drawn some attention recently [5–7]. It has been pointed out that the effect of 'structural' change in the solvent, brought about by an alcohol, is of paramount influence on such kinetics [5–7].

The physical properties of the aqueous solutions of alcohols have been studied extensively and comprehensive review articles are available [8, 9]. Recent studies using various modern techniques have advanced the understanding of the nature of aqueous solutions of alcohols considerably [10–19]. These results are no doubt useful in understanding the mixed solvent effect on reactions in aqueous solutions.

In view of the above situation, we studied the kinetics of the isomerization of *trans*-bis(oxalato)diaquachromate(III) in aqueous tert-butanol and ethanol solutions. Since the key issue is an effect of the mixed solvent, and the strategy is to utilize the accumulated knowledge about the physical properties of these aqueous solutions [8–19], the alcohol solutions used here were neither buffered nor their ionic strengths controlled, which is customary in kinetic studies. Otherwise, there would have been added complications on the nature of the solutions due to the presence of electrolytes.

It turned out that there was a strong effect of mixed solvent on these isomerization kinetics. While the results presented here are preliminary in nature, it is felt worthwhile to report our findings.

Experimental

K[*trans*-$Cr(C_2O_4)_2(H_2O)_2$]·$3H_2O$ was prepared by the conventional method [20]. The tert-butanol (BDH, assured) and ethanol (Stanchem, anhydrous) used were analysed by analytical gas chromatography. The purities of both alcohols were higher than 99.9%. D_2O of purity 99.7% was purchased from MSD Isotopes and was used without further purification.

The solutions were prepared by weight, and preheated to the desired temperature prior to the kinetic runs. An amount of finely powdered *trans*-complex salt was dissolved to make the concentration in the range from 0.01 to 0.05 M. Typically, the pH value measured by a glass electrode of the resulting solution was about 5. The kinetics were followed by the change in the absorbance at 416 nm by means of a Perkin-Elmer Lambda 3B spectrophotometer. The temperature of the cuvette holder was controlled within ±0.5 °C, and was measured by means of a thermocouple immersed directly in the cuvettes. The cuvettes were sealed with a piece of parafilm to retard evaporation of the solvent.

While the aquation of tris(oxalato)chromate(III) to *cis*-bis(oxalato)diaquachromate(III) is known to proceed with about the same half-life as the present isomerization reaction, no further aquation was detected in an acidic medium at room temperature [21]. It is therefore expected that solvolysis in alcohols does not occur at a detectable rate. Indeed, the absorption spectra of the final product in mixed solvents were identical with that in water.

The apparent first-order rate constants, k_{obs}, were obtained as the slopes of the plots of $\ln(A_\infty - A)$ against time, where A_∞ is the absorbance at the completion of the reaction. Such plots gave a good straight line for at least 2.5 times the half-life.

Results and Discussion

The values of k_{obs} are tabulated in Table 1. The values in pure H_2O were the same within the experimental error as those of k_1 in ref. 4, which is the rate constant for the process of the isomerization purely from *trans*-bis(oxalato)diaquachromate(III) to the *cis*

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TABLE 1. Rate constants, k_{obs}

xH_2O	$[H_2O]$ (mol l^{-1})	a_{H_2O} (mol l^{-1})	k_{obs} (min^{-1})
tert-Butanol, 31 °C			
1.0000	55.21		0.0560
0.9797	50.26		0.0465, 0.0417
0.9796	50.24		0.0447
0.9595	45.99		0.0400
0.9577	45.64		0.0342, 0.0315
0.9546	44.53		0.0265
0.9511	44.34		0.0310
0.9451	43.21		0.0285, 0.0269
0.9418	42.60		0.0292
0.9241	39.48		0.0250, 0.0235
0.9221	39.15		0.0275
0.8965	35.22		0.0217, 0.0263
0.8598	30.55		0.0251
tert-Butanol, 36 °C			
0.9900	52.59		0.0790
0.9787	49.96		0.0700, 0.0696
0.9704	48.10		0.0531
0.9607	46.12		0.0535, 0.0513
0.9425	42.60		0.0415, 0.0444
0.9333	40.90		0.0344
0.9244	39.39		0.0369, 0.0400
0.9043	36.20		0.0344, 0.0329
0.8619	30.63		0.0238
0.8100	25.21		0.0239
tert-Butanol, 41 °C			
1.0000	55.00		0.133
0.9902	52.51		0.127
0.9704	48.00		0.0864
0.9518	44.21		0.0690
0.9329	40.70		0.0642
0.8888	33.87		0.0488
0.8619	30.50		0.0346
0.8100	25.09		0.0300
Ethanol, 35 °C			
1.0000	55.19		0.0673
0.9802	51.95		0.0568
0.9619	49.08		0.0467
0.9440	46.65		0.0360
0.9273	44.65		0.0369
0.9189	43.50		0.0321
0.9184	43.49		0.0356
0.9113	42.67		0.0308
0.9106	42.65		0.0283
0.8735	38.43		0.0227
0.7852	30.10		0.0117
Ethanol, 30 °C			
1.0000	55.25	55.25	0.0471, 0.0485
0.9849	52.55	52.58	0.0400, 0.0424
0.9684	50.30	50.40	0.0388
0.9561	48.35	48.57	0.0304, 0.0311
0.9374	45.87	46.15	0.0263, 0.0273
0.9070	42.25	42.80	0.0202, 0.0201
0.8730	38.35	39.30	0.0160
0.8381	34.82	36.32	0.0129
0.8091	32.34	34.40	0.0077
0.7832	29.95	32.50	0.0073

form without any formation, and hence participation in the isomerization, of the corresponding hydroxy complexes. The activation energy and the activation entropy for the present work (74 ± 2 kJ mol^{-1} and 54 ± 7 J K^{-1} mol^{-1}) compare well with those of ref. 4 (75.7 ± 0.5 kJ mol^{-1} and 53.5 ± 1.6 J K^{-1} mol^{-1} respectively).

To see the isotope effect, twelve pairs of runs, one in H_2O and the other in D_2O, were performed at 30.0 °C using a multicuvette holder. The ratios of the value of k_{obs} in D_2O over that in H_2O were 0.965, 0.965, 0.969, 0.969, 1.00, 1.00, 1.01, 1.05, 1.09, 1.11, 1.13 and 1.15. The average is 1.03 ± 0.06 at the 99% confidence level. Thus it appears that solvent water does not play an active role in the rate-determining step. While it is not directly relevant to the present system, the ratio in the rates of aquation of $[Co(NH_3)_5Cl]^{2+}$ was found to be about 0.65 [22]. This fact together with other evidence supports a mechanism that is almost S_N2 but includes the active participation of NH_3 ligands via hydrogen bonds to solvent water molecules [22]. Thus, if there were an S_N2-type participation of water molecules in the present isomerization reaction, the measured ratio would have been much more significantly different from what was observed.

When alcohol was added to water, the value of k_{obs} decreased dramatically. The plots of $\ln(k_{obs})$ against $\ln[H_2O]$ are shown in Fig. 1 for the tert-butanol–water solutions and those for ethanol–water in Fig. 2. The concentrations in the mixtures were calculated using the literature values of densities of the respective solutions [23, 24]. Since activity coefficient data are available for the ethanol–water system [25], the plots of $\ln(k_{obs})$ against $\ln(a_{H_2O})$ at 30 °C are also shown in Fig. 2, where a_{H_2O} is the activity of H_2O. Scatters of the plots may be due to the fact that the amount of the complex dissolved was not controlled. This resulted in a small variation in the pH value of the resulting solution. As pointed out in ref. 4, the value of pH ≈ 5 is about the threshold above which the apparent rate changes sharply.

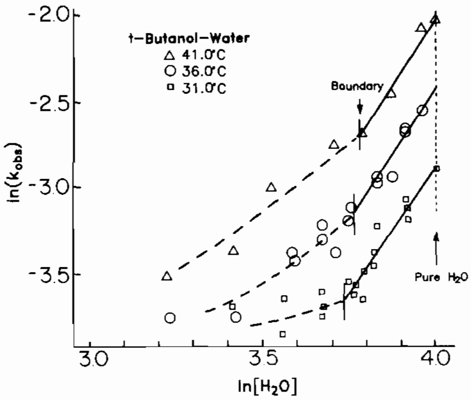

Fig. 1. $\ln(k_{obs})$ against $\ln[H_2O]$ for the tert-butanol–water media. The vertical lines show the boundaries of the water-rich region; see the text.

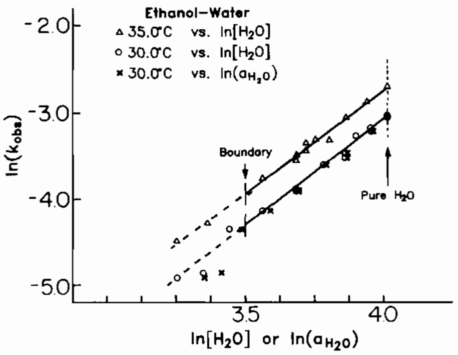

Fig. 2. $\ln(k_{obs})$ against $\ln[H_2O]$ or $\ln(a_{H_2O})$ for the ethanol–water media. The vertical lines show the boundaries of the water-rich region; see the text.

For the tert-butanol–water solutions, it has been concluded that up to a certain boundary value in the mole fraction, x_{TBA}, tert-butanol molecules enhance the hydrogen bond network of water all through its entire bulk [11, 12]. Namely, an added tert-butanol molecule forces the surrounding water molecules to form more hydrogen bonds than in pure water. This effect reaches a very long range via the hydrogen bond network inherent to liquid water. As the concentration of tert-butanol increases, this structure enhancement increases sharply up to the boundary value, beyond which the mode of mixing becomes completely different. Such boundaries were reported to be at $x_{TBA} = 0.06$, 0.055 and 0.05 for 30.00, 45.17 and 59.49 °C respectively [11, 12]. For the ethanol–water mixtures, the same argument can be applied using the data of the partial molar enthalpies of ethanol in aqueous solutions [26], with an estimated boundary value, $x_{ethanol} = 0.2$. Thus, in the water-rich region below the boundary, the effect of alcohol on the nature of solvent water can be looked upon as making the hydrogen bonding capability of the latter less available to the added complex ions. Obviously, complex ions themselves should have a significant effect on the nature of the solution. As a first approximation, however, such an effect can be regarded as a small perturbation, since the concentration of the complex ion is small: 0.01 to 0.05 M in comparison with about 2 M for tert-butanol at $x_{TBA} = 0.05$, for example.

As shown in Figs. 1 and 2, in the water-rich region down to the boundary, k_{obs} varies as $[H_2O]^{\alpha}$, with $\alpha = 2.9$ for tert-butanol–water and $\alpha = 3.1$ for ethanol–water. The fact that these plots at different temperatures are on parallel straight lines to each other means that the activation energies in this region are the same as that in pure water. These findings suggest that the same mechanism is operative in this region as in pure water and that three water molecules take part in the rate-determining step. The latter suggestion is in apparent contradiction to the lack of isotope effect.

A plausible explanation is that the five-membered coordination species is stabilized by three water molecules via hydrogen bonding. Thus, when alcohols are added, hydrogen bonds become less available to stabilize the five-membered coordination species. While there are suggestions that the strength in the hydrogen bond network for D_2O is slightly stronger than that in H_2O [27–29], the difference may be too small to manifest itself in the present measurement. However, there is evidence that such a difference between D_2O and H_2O does not exist in solution [30]. The lack of an isotope effect suggests that the subsequent step of exchange of the open-end of the oxalate ion with an adjacent water ligand takes place unimolecularly, without the participation of water.

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