

THE ARRHENIUS PARAMETERS FOR THE REPLACEMENT OF THE  
FIRST COORDINATED CHLORINE FROM THE *trans*-DICHLOROBIS-  
(ETHYLENEDIAMINE)COBALT(III) CATION BY SOLVENT WATER\*

By S. C. CHAN†

The activation energy for the solvolytic aquation of the *trans*-dichlorobis-(ethylenediamine)cobalt(III) cation has been reported severally by Mathieu<sup>1</sup> ( $E_{\text{act}}$  24.2 kcal/mole), Pearson *et al.*<sup>2</sup> ( $E_{\text{act}}$  28 kcal/mole), and Panasyuk *et al.*<sup>3</sup> ( $E_{\text{act}}$  27.85 kcal/mole), but discrepancies existed among these results. Although the American workers<sup>2</sup> claimed that accurate and pH-independent results can be obtained only at pH < 3 (which has been confirmed by us), the Russian workers<sup>3</sup> used a pH of 4.5 in their kinetic studies. In connection with our programme for comparing the kinetics of substitutions of *trans* complexes in the bis(propylenediamine)cobalt(III) system with those of the corresponding ethylenediamine analogues, exact information on this aspect was required. The present work was therefore initiated to check the large difference between the values previously reported by the various sets of workers. It shows that the temperature dependence of the rate constants reported below (in the Experimental section) can be satisfactorily expressed by

$$k = 1.1 \times 10^{15} \exp(-26700/RT) \text{ sec}^{-1}$$

and so the value of  $(dE_{\text{act}}/dT)_p$ , and hence  $\Delta C_p$ , for this reaction is not very different from zero. In unimolecular solvolysis of *trans* complexes of the chloroamminecobalt(III) system in aqueous solutions, the partial desolvation resulting from a change in geometry (from octahedral to trigonal bipyramidal) acts in opposition to the solvation of the developing chloride ion, and these two effects, taken jointly, may explain the fortuitous applicability of the two-constant equation of Arrhenius over a temperature range of 50°. The activation energy obtained in the present investigation is significantly higher than that given by Mathieu, and somewhat lower than those of Pearson or of Panasyuk.

### Experimental

#### Preparation

*trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride was prepared by a method similar to that of Bailar<sup>4</sup> except that the oxidation of the aqueous solution of cobalt(II) chloride hexahydrate (160 g in 500 ml water) was carried out with 30% hydrogen peroxide (67 ml).

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† Department of Chemistry, University of Hong Kong, Hong Kong.

<sup>1</sup> Mathieu, J. P., *Bull. Soc. chim. Fr.*, 1936, **3**, 2152.

<sup>2</sup> Pearson, R. G., Boston, C. R., and Basolo, F., *J. Am. chem. Soc.*, 1953, **75**, 3089.

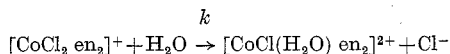
<sup>3</sup> Panasyuk, V. D., Solomko, V. P., and Reiter, L. G., *Russ. J. inorg. Chem.*, 1961, **6**, 1033.

<sup>4</sup> Bailar, J. C., *Inorg. Synth.*, 1946, **2**, 222.

The crude product was purified by crystallization from the minimum amount of water at 35°, the purity being checked by chloride analysis.

### Kinetics

The progress of the reaction



was followed by titrating the chloride ion liberated (Volhard), after the complex cation was removed by a cation exchange resin column (Amberlite IR-120;  $\text{H}^+$  form). The replacement of the second coordinated chlorine is retarded by acid and in 0.01N nitric acid, the two steps could be separated from one another. The reaction solutions were made up by dissolving a weighed amount ( $4 \times 10^{-3}\text{M}$ ) of the complex in 0.01N nitric acid previously brought to the temperature of the reaction. For temperatures below 25°, samples were withdrawn from time to time and passed directly through the resin for analysis. At higher temperatures, the samples were first rapidly frozen and then melted at 0° before being delivered into the resin. In both cases the resin column was surrounded by ice-water, and continually flushed with water between

TABLE I  
RATE CONSTANTS FOR THE REPLACEMENT OF THE FIRST COORDINATED  
CHLORINE FROM *trans*-DICHLOROBIS(ETHYLENEDIAMINE)COBALT(III)  
CATION BY SOLVENT WATER AT VARIOUS TEMPERATURES

Temp.	$k$ (sec <sup>-1</sup> )	Temp.	$k$ (sec <sup>-1</sup> )
0.0°	$5.6 \times 10^{-7}$	30.0	$7.3 \times 10^{-5}$
5.0	$1.35 \times 10^{-6}$	35.0	$1.51 \times 10^{-4}$
10.0	$3.18 \times 10^{-6}$	40.0	$3.03 \times 10^{-4}$
15.0	$7.3 \times 10^{-6}$	45.0	$6.0 \times 10^{-4}$
20.0	$1.61 \times 10^{-5}$	50.0	$1.15 \times 10^{-3}$
25.0	$3.48 \times 10^{-5}$		

separations. The first-order rate constants were determined from the slopes of the plots of  $\log_{10}(V_\infty - V_t)$  against time, where  $V_t$  is the titre of silver nitrate consumed at time  $t$ , and  $V_\infty$  is the corresponding value calculated from the weight of complex taken, assuming complete replacement of one coordinated chlorine only. The results are collected in Table I, where the value given for each complex at each temperature represents the average of three constants, determined from separate runs, which agree to better than  $\pm 1\%$ .

At 0°, the thermostat was a large Dewar flask filled with crushed ice and water. Other thermostats used were of the conventional design capable of holding temperatures constant to  $\pm 0.05^\circ$ . Light was carefully excluded from the reaction mixture as a routine precaution.

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